



Concise Explanation of documents

Excerpted English translation of JP-A-11-222641

From line 1 in column 1 to line 6 in column 2 on page (2)

[Claims]

[Claim 1] A copper alloy for conductive springs, containing, as main components, 1.0 to 3.5 wt% of Ni, 0.2 to 0.9 wt% of Si, 0.01 to 0.20 wt% of Mg, and 0.05 to 1.5 wt% of Sn, with S and O in a content restricted to less than 0.005 wt% respectively, with the balance being Cu and inevitable impurities, and having a crystal grain size of more than 1 μm and 25 μm or less.

[Claim 2] A copper alloy for conductive springs, containing, as main components, 1.0 to 3.5 wt% of Ni, 0.2 to 0.9 wt% of Si, 0.01 to 0.20 wt% of Mg, 0.05 to 1.5 wt% of Sn and 0.2 to 1.5 wt% of Zn, with S and O in a content restricted to less than 0.005 wt% respectively, with the balance being Cu and inevitable impurities, and having a crystal grain size of more than 1 μm and 25 μm or less.

[Claim 3] The copper alloy for conductive springs according to claim 1 or 2, wherein the copper alloy further contains 0.005 to 2.0 wt% in total of one or more elements selected from 0.005 to 0.3 wt% of Ag, 0.01 to 0.5 wt% of Mn, 0.005 to 0.2 wt% of Fe and Cr respectively, 0.05 to 2.0 wt% of Co, and 0.005 to 0.1 wt% of P.

[Claim 4] The copper alloy for conductive springs according to claim 1 or 2, wherein the copper alloy further contains 0.005 to 0.13 wt% in total of one or two elements selected from 0.005 to 0.1 wt% of Pb and 0.005 to 0.03 wt% of Bi.

[Claim 5] The copper alloy for conductive springs according to claim 1 or 2, wherein the copper alloy further contains 0.005 to 2.0 wt% in total of one or more elements selected from 0.005 to 0.3 wt% of Ag, 0.01 to 0.5 wt% of Mn, 0.005 to 0.2 wt% of Fe and Cr respectively, 0.05 to 2.0 wt% of Co, and 0.005 to 0.1 wt% of P and one or two components selected 0.005 to 0.1 wt% of Pb and 0.005 to 0.03 wt% of Bi.

[Claim 6] The copper alloy for conductive springs according to any one of claims 1 to 5, wherein the alloy is used for any of terminals, connector materials, and switch materials.

[Claim 7] A manufacturing method of the copper alloy for conductive springs according to any one of claims 1 to 6, wherein recrystallization treatment is carried out at 700 to 920°C after cold working.

[Claim 8] A manufacturing method of the copper alloy for conductive springs according to any one of claims 1 to 6, wherein recrystallization treatment is carried out at 700 to 920°C after cold working, and then aging treatment is

carried out at 420 to 550°C.

[Claim 9] A manufacturing method of the copper alloy for conductive springs according to any one of claims 1 to 6, wherein recrystallization treatment is carried out at 700 to 920°C after cold working, cold working with a reduction of 25% or less is further carried out, and then aging treatment is carried out at 420 to 550°C.

[Claim 10] A manufacturing method of the copper alloy for conductive springs according to any one of claims 1 to 6, wherein recrystallization treatment is carried out at 700 to 920°C after cold working, cold working with a reduction of 25% or less and then aging treatment at 420 to 550°C are carried out, and further cold-working with a reduction of 25% or less and low-temperature annealing are carried out.

From line 21 to 25 in column 10 on page (6)

[0031]

[Best Mode for Carrying out the Invention]

A copper alloy of the present invention has excellent mechanical strength, bending property, stress relaxation property, resistance to Sn-plating peeling, and punching suitability, and especially has properties required for a common conductive material such as terminal-connector materials, switch materials, relay materials, and the like; and the alloy will be described

in detail referring to examples.

From line 12 to 17 in column 12 on page (7) and Table 1
[0039]

The thermal peeling resistance of the Sn plating was evaluated in the following manner. A test piece of each of the sample sheets was subjected to a glossy tin plating with a thickness of 1 μm , and the resultant test piece was heated at 150°C for 1,000 hours in atmospheric air, followed by 180-degree contact bending and bending back. After that, the peeling of the plating at the bent portion was observed with the naked eye. In the case solder peeling was observed, a word, existing, was written in Tables 4 to 6.

[Table 1]

This invention	No.	Ni	Si	Mg	Sn	Zn	S	O	Others	Grain size
	1	1.5	0.34	0.07	0.31	0.49	0.002	0.001		5
	2	1.9	0.48	0.08	0.30	0.48	0.002	0.001		↑
	3	2.5	0.60	0.08	0.30	0.49	0.002	0.001		↑
	4	3.0	0.75	0.07	0.31	0.50	0.002	0.001		↑
	5	2.0	0.48	0.04	0.30	0.50	0.002	0.001		↑
	6	1.9	0.48	0.03	0.85	0.49	0.002	0.001		↑
	7	2.0	0.47	0.08	0.87	0.50	0.002	0.001		↑
	8	2.0	0.46	0.16	0.29	0.09	0.002	0.001		↑
	9	2.0	0.47	0.16	0.30	1.10	0.002	0.001		↑
	10	2.0	0.48	0.08	0.30	1.07	0.002	0.001		↑
	11	1.9	0.46	0.04	0.87	0.10	0.002	0.001		↑
	12	2.0	0.48	0.07	0.85	1.10	0.002	0.001		↑
	13	1.5	0.47	0.08	0.33	0.50	0.002	0.001	Co 0.5	↑
	14	1.9	0.48	0.08	0.31	0.49	0.002	0.001	Co 0.1	↑
	15	2.0	0.48	0.08	0.32	0.49	0.002	0.001	Ag 0.03	↑
	16	2.0	0.48	0.07	0.32	0.49	0.002	0.001	Pb 0.03	↑
	17	2.0	0.47	0.08	0.33	0.50	0.002	0.001	Cr 0.007	↑
	18	1.9	0.48	0.07	0.32	0.48	0.002	0.001		2
	19	2.0	0.48	0.06	0.33	0.49	0.002	0.001		10
	20	2.0	0.46	0.08	0.33	0.50	0.002	0.001		15
	21	1.9	0.48	0.08	0.31	0.50	0.002	0.001		20

Concise explanation with respect to JP-A-11-222641

If heat/electric conductivity of an alloy is poor, stress relaxation is accelerated due to heating of the alloy itself. Accordingly, the balance between conductivity and stress relaxation property is necessarily considered. JP-A-11-222641 describes a copper alloy developed by the present inventors and others, which alloy satisfy the balance between conductivity and stress relaxation property. However, with respect to the alloy in JP-A-11-22641, there is room for further improvement in compatibility to plating and in resistance to deterioration of plate after plating (which are collectively called as plating characteristics).

Excerpted English translation of JP-A-11-256256

From line 1 in column 1 to line 3 in column 2 on page (2)

[Claims]

[Claim 1] A copper alloy for electric and electronic parts excellent in stamping workability, comprising 0.1-4.0 wt% of Ni, 0.01-1.0 wt% of Si, 0.01-5.0 wt% of Zn, 0.005 or less wt% of S, and 0.005 or less wt% in total of one or more elements selected from the following group consisting of 0.003 wt% or less of Se, 0.003 wt% or less of Te, 0.003 wt% or less of Sb, and 0.003 wt% or less of Bi, with the balance being Cu and inevitable impurities.

[Claim 2] A copper alloy for electric and electronic parts excellent in stamping workability, comprising 0.1-4.0 wt% of Ni, 0.01-1.0 wt% of Si, 0.01-5.0 wt% of Zn, 0.0001-0.005 wt% of S, and 0.00003-0.005 wt% in total of one or more elements selected from the group consisting of 0.00003-0.003 wt% of Se, 0.00003-0.003 wt% of Te, 0.00003-0.003 wt% of Sb, and 0.00003-0.003 wt% of Bi, with the balance being Cu and inevitable impurities.

[Claim 3] A copper alloy for electric and electronic parts excellent in stamping workability according to claim 1 or 2, further containing 0.0001-0.05 wt% in total of one or two elements selected from the group consisting of 0.0001-0.05 wt% of Pb and 0.0001-0.01 wt% of C.

[Claim 4] A copper alloy for electric and electronic parts excellent in stamping workability according to any one of claims 1 to 3, further containing 0.0001-0.3 wt% in total of one or two elements selected from the group consisting of 0.0001-0.1 wt% of P and 0.0005-0.3 wt% of Al.

[Claim 5] A copper alloy for electric and electronic parts excellent in stamping workability according to any one of claims 1 to 4, further containing 0.001-1.5 wt% of Mg.

[Claim 6] A copper alloy for electric and electronic parts excellent in stamping workability according to any one of claims 1 to 5, further containing 0.0003-0.7 wt% in total of one or more elements selected from the group consisting

of 0.001-0.5 wt% of Mn, 0.001 wt% or more but less than 0.03 wt% of Fe, 0.001-0.1 wt% of Co, 0.0003-0.1 wt% of Ag, 0.0005-0.01 wt% of Cr, 0.0005-0.01 wt% of Zr, and 0.0005-0.01 wt% of Ti.

[Claim 7] A copper alloy for electric and electronic parts excellent in stamping workability according to any one of claims 1 to 6, further containing oxygen in a content of 30 ppm or less and hydrogen in a content of 10 ppm or less.

[Claim 8] A copper alloy for electric and electronic parts excellent in stamping workability according to any one of claims 1 to 7, further containing 0.01-8.0 wt% of Sn.

From line 37 in column 8 on page (5) to line 8 in column 9 on page (6)

[0025] A lead frame, for which the alloy of the present invention finds utility, is heated at 200 to 350°C in the step of mounting-packaging an Si chip. In the step of wire bonding, in order to prevent oxidation at the time of heating, usually the heating is performed in a non-oxidative atmosphere such as a nitrogen-hydrogen mixed gas. However, because of difficulty of completely preventing the penetration of air into the heating furnace, or because of prolongation of its residence time in the furnace, for example, in case of the occurrence of stopping of the line due to unexpected matter, the lead frame undergoes oxidation by the penetrating air. If the

adhesion strength between the oxide film produced on the surface of the lead frame and the matrix is low, after resin molding, moisture will penetrate through a gap formed when the oxide film is peeled off from the matrix so that the reliability of the IC is considerably decreased. For this reason, when the alloy is used for a lead frame, adhesion of its oxide film is one of important prescribed properties. With respect to surface roughness of the alloy of the present invention, if the center line average roughness (Ra) exceeds $0.2\ \mu\text{m}$ or the maximum height (Rmax) exceeds $1.0\ \mu\text{m}$, the adhesion of the oxide film is decreased. In consideration of this, it is desirable that with respect to the surface roughness, Ra is $0.2\ \mu\text{m}$ or less and Rmax is $1.0\ \mu\text{m}$ or less. Then, when the surface roughness satisfies these conditions, no problem occurs in plating suitability, bending workability, and the like, so that the alloy is suitable for electric and electronic parts such as a lead frame, a terminal and a connector.

From line 45 in column 24 on page (13) to line 5 in column 26 on page (14)

[0058] <Test Method> Influences of surface roughness on the adhesion of oxide film were examined by the following methods.

[Surface Roughness] Each test piece subjected to

ultrasonic cleaning with acetone was measured of its roughness by scanning a probe parallel to the direction of rolling over a length of 5 mm. Five test pieces for each sample exhibited approximately the same surface roughness. As the surface roughness of each sample, an average value of data on the five test pieces was used. For the measurement of surface roughness, a stylus type surface roughness measuring apparatus (produced by Taylor Hobson) was used. Note that the definition of surface roughness was according to JIS-B0601 (Definition of and indication of surface roughness).

[0059] [Adhesion of Oxide Film] On a hot plate (HOT PLATE HHP-401, produced by SEFI Co.) kept at 300°C were placed test pieces of respective surface roughness values and heated for 30 minutes. After predetermined period of time, the test pieces were cooled to room temperature, then a commercially available acetate adhesive tape (3M No. 810) was applied thereto and immediately peeled off therefrom. Presence or absence of attachment of the oxide film onto the adhesive surface of the tape was examined by visual observation. No attachment of oxide film to the adhesive surface was evaluated as O, and any attachment of oxide film thereto was evaluated as X. Note that the heating test with the hot plate, and peeling off test were performed in a chamber at 25°C and at relative humidity of

60%.

[0060] [Test Results] Results obtained are shown in Table 10.

[0061]

[Table 10]

Table 10: Relationship between Surface Roughness and Peeling of Oxide Film

No.	Ra μm	Rmax μm	Peeling of oxide film
27-7	0.06	0.35	○
27-8	0.12	0.74	○
27-9	0.25*	1.16	×
27-10	0.44*	2.8	×

[0062] In No. 27-7 and No. 27-8 having Ra of 0.2 μm or less and Rmax of 1.0 μm or less with respect to a surface roughness, the oxide film did not peel off, while in No. 27-9 and No. 27-10 whose surface roughness exceeded the above-mentioned range, the oxide film peeled off.

Excerpted English translation of JP-A-5-59468

From lines 1 to 25 in column 1 on page (2)

[Claims]

[Claim 1] A copper alloy for conductive springs, comprising 0.5-4.0 % (means wt%, hereinafter the same) of

Ni, 0.1-1.0 % of Si, 0.01 to 0.1 % of Mg, 0.0015 % or less of S, 0.0015 % or less of O, and the balance of Cu.

[Claim 2] A copper alloy for conductive springs, comprising 0.5 to 4.0% of Ni, 0.1 to 1.0% of Si, 0.01 to 0.1% of Mg, 0.01 to 15% of Zn, 0.0015% or less of S, 0.0015% or less of O, and the balance of Cu.

[Claim 3] A copper alloy for conductive springs, comprising 0.5 to 4.0% of Ni, 0.1 to 1.0% of Si, 0.01 to 0.1% of Mg, 0.0015% or less of S, 0.0015% or less of O, further, as auxiliary components, 0.005 to 1.0% of one or more elements selected from P, B, As, Fe, Co, Cr, Al, Sn, Ti, Zr, In and Mn, and the balance of Cu.

[Claim 4] A copper alloy for conductive springs, comprising 0.5 to 4.0% of Ni, 0.1 to 1.0% of Si, 0.01 to 0.1% of Mg, 0.01 to 15% of Zn, 0.0015% or less of S, 0.0015% or less of O, further, as auxiliary components, 0.005 to 1.0% of one or more elements selected from P, B, As, Fe, Co, Cr, Al, Sn, Ti, Zr, In and Mn, and the balance of Cu.

From line 35 to 42 in column 7 on page (5)

Regarding the thermal peeling resistance of a tin plating, each specimen, which was plated with a 0.5 to 0.8 μm -thick copper underplating, further plated with a 1 to 1.5 μm -thick tin by electroplating, and then subjected to thermal reflow, was cut into 10 mm W \times 100 mm L, heated

at 150°C for a prescribed period (at every 100 hours), subjected to 90° bending back and forth one time in one side with a curvature of 0.3 mm (= the plate thickness), and the peripheral part of the bent part in the front and the rear faces was observed with a visual field enlarged 20 times, to confirm the occurrence of peeling of the plating.

Concise explanation with respect to JP-A-5-59468

JP-A-5-59468 shows effectiveness of Mg added to a Cu alloy to improve stress relaxation property. However, although stress relaxation property is improved by the addition of mg, this alloy material is poor in bending property, to cause cracks upon subjected to 180°-contact bending test, and the like. Accordingly, this alloy is necessarily improved in bending property to be used as a connector for automobile and the like.

Excerpted English translation of JP-A-1-180932

From line 4 to line 14 in column 1 on page (1)

[Claim]

[Claim 1] A highly tensile and highly electrically conductive copper alloy for pin grid array IC lead pins comprising 3.0 to 3.5 wt% of Ni, 0.5 to 0.9 wt% of Si, 0.05 to 5 wt% of Zn, 0.2 to 2.0 wt% of Sn, 0.001 to 0.1 wt% of Cr, 0.001 to 0.01 wt% of Mg, and the balance of Cu

and inevitable impurities, and having Vickers hardness of 200 or more and electrical conductivity of 30% IACS or more after a soft brazing treatment at lower than 450°C, and being excellent in the heat resistance, the stiffness strength, the repeated bendability and the noble metal platability.

From line 19 in lower right column on page (3) to line 2 in upper left column on page (4)

(6) The adhesion property of the Au plating was investigated by forming a 2 μ m-thick Ni underlayer plating and a 3 μ m-thick Au plating, heating at a brazing temperature of 425°C for 15 minutes, and then observing the occurrence of the blister with a magnifier.

Excerpted English translation of JP-A-6-100983

From line 1 to line 47 in column 1 on page (2)

[Claims]

[Claim 1] A metal foil for a TAB tape having high young modulus and high yield strength, wherein the metal foil is an alloy containing 20 to 95 wt% of Cu, 0.3 to 11 wt% of Al, 0.05 to 3.0 wt% of Mn, 0.005 to 3.5 wt% of Ti, 0.5 to 10 wt% of Cr, 0.001 to 1.5 wt% of Mo, and the balance of Fe and inevitable impurities, and has an aspect ratio of crystal grain size (the ratio of the crystal grains in the rolling direction and the perpendicular direction to

rolling) of 20 or less, and a foil thickness of 80 μm or less.

[Claim 2] The metal foil according to claim 1, wherein the weight ratio of Cr content to Fe content is 5.5 to 13.5 %.

[Claim 3] The metal foil according to claim 1 or 2, wherein the alloy further contains, as alloying elements, 0.005 to 8 wt% in total of one or more elements selected from Zr, Si, Ni, Zn, Sn, Nb, P, La, Ce, Y, V, Ca, Be, Mg or Hf, and 0.005 to 2 wt% in total of one or more of C or B.

[Claim 4] The metal foil according to any one of claims 1 to 3, wherein a surface of the metal foil is plated in a thickness of 0.001 to 0.02 μm , with a Ni, Cu, Ag, Au or their alloy plating, a Sn-Pb plating, or a tin plating in a single or a plurality of layers.

[Claim 5] A manufacturing method of a metal foil for a TAB tape having high young modulus and high yield strength, which foil has and slight characteristic anisotropy and is excellent in lead deformation resistance and heat resistant strength, wherein the method comprises steps of melting and casting an alloy with the composition according to any one of claims 1 to 3, and then hot-rolling the cast at a temperature in a range of 700 to 1,000°C, primarily cold-rolling the resulting plate with a reduction ratio of 50 to 95%, annealing the resulting

sheet at a temperature in a range of 800 to 1,000°C, and then secondarily cold-rolling the sheet with a reduction ratio of 1 to 70%, further subjecting the resulting foil to solution heat treatment at a temperature in a range of 700 to 1,000°C and then quenching the foil, and successively aging the foil at a temperature in a range of 350 to 650°C.

[Claim 6] A manufacturing method of a metal foil for a TAB tape having high young modulus and high yield strength, which foil has slight characteristic anisotropy and is excellent in lead deformation resistance and heat resistant strength, wherein the method comprises steps of melting and casting an alloy with the composition according to any one of claims 1 to 3, and then hot-rolling the cast at a temperature in a range of 700 to 1,000°C, primarily cold-rolling the hot-rolled plate with a reduction ratio of 50 to 90%, annealing the resulting sheet at a temperature in a range of 800 to 1,000°C and successively quenching the sheet, and then secondarily cold-rolling the sheet with a reduction ratio of 1 to 70%, and further successively aging the resulting foil at a temperature in a range of 350 to 650°C.

[Claim 7] The manufacturing method according to claim 5 or 6, wherein the secondary cold-rolling is carried out with a reduction ratio of 1 to 15%.

[Claim 8] The manufacturing method according to any one of claims 5 to 7, wherein the metal foil after the aging treatment is plated with a Ni, Cu, Ag, Au or their alloy plating, a Sn-Pb plating, or a tin plating with a thickness of 0.001 to 0.02 μm , in a single or a plurality of layers.

From line 33 to line 41 in column 14 on page (8)

[0024] Example 2

Table 5 shows the evaluation results of materials obtained by processing the specimens C, P shown in Table 1 and Table 2 with the following steps. That is, after 1 mm-thick metal plates obtained by hot-rolling were subjected to surface-grinding, the plates were subjected to primary cold-rolling with a reduction ratio of 35 to 96% to obtain sheets with a thickness of 0.055 mm, and the sheets were annealed at 1,000°C for 60 seconds, cooled at 100°C/min cooling rate with nitrogen gas, and then subjected to secondary cold-rolling of 1 to 75%.

[Table 5]

Sample No.	Specimens		Ratio of the primary cold rolling (%)	Ratio of the secondary cold rolling (%)	Aspect ratio	Yield strength (Kgf/mm ²)		Conductivity (%IACS)		Workability	
						L	C	L	C	L	C
31	C	Comparative example	35	1	1.3	80	80	63	63	O	Δ
32	C	This invention	55	1	1.7	82	80	65	63	O	O
33	C	This invention	60	5	2.8	81	80	65	63	O	O
34	C	This invention	90	20	12.5	82	81	65	63	O	O
35	C	This invention	93	30	17.5	85	83	65	62	O	O
36	C	Comparative example	96	75	23.5	87	75	65	58	O	O
37	P	Comparative example	35	1	1.3	80	80	63	66	O	Δ
38	P	This invention	55	1	1.7	81	80	65	66	O	O
39	P	This invention	60	5	2.8	81	80	67	65	O	O
40	P	This invention	90	20	12.5	82	81	67	66	O	O
41	P	This invention	93	30	17.5	83	83	67	65	O	O
42	P	Comparative example	96	75	23.5	83	73	68	60	O	O

Concise explanation with respect to JP-A-61-127842

JP-A-61-127842 describes a Cu-Ni-Si-series alloy as a copper-series material that satisfies requirements under a severe condition of a high temperature and corrosive environment. However, such a Cu-Ni-Si-series alloy also has lapsed into an unusable state. More specifically, miniaturization of parts, for example, in a general box-type terminal, the reduction in tab width of a male terminal to be inserted of from about 2 mm to about 1 mm results in a decrease in the width of a spring part to about 1 mm, which is difficult to give a sufficient connection strength. Further, as correlated with the miniaturization, to secure connection strength at a spring part, many studies have been made on the structure of terminals. As a result, bending property required to a material has become more and more severe, and the conventional Cu-Ni-Si-series alloy often causes cracks at the bent portion. It is similarly applicable to stress relaxation property. Accordingly, the conventional Cu-Ni-Si-series alloy cannot be used for a long period of time, due to the increase of stress applied to the material and the change of environment to be used to become a higher temperature.

Excerpted English Translation of JP-A-11-43731

From line 1 in column 1, to line 40 in column 2, on page
(2)

[Claims]

[Claim 1] A high strength copper alloy excellent in stamping workability and suitable for silver plating, comprising 0.4-4.0 wt% of Ni, 0.05-1.0 wt% of Si, 0.001-5.0 wt% of Sn, 0.1-5.0 wt% of Zn, 0.005-1.0 wt% of Mg, 0.0003-0.005 wt% of S, 0.0003-0.01 wt% of C and the balance of Cu with inevitable impurities, wherein respective contents of Mg and S simultaneously satisfy the following inequalities (1) and (2):

$$0.5[\text{Mg}] + [\text{S}] \geq 0.005 \dots(1)$$

$$0.25[\text{Mg}] \geq [\text{S}] \dots(2)$$

([Mg] means wt% of Mg and [S] means wt% of S, hereinafter the same.)

[Claim 2] A high strength copper alloy excellent in stamping workability and suitable for silver plating, comprising 0.4-4.0 wt% of Ni, 0.05-1.0 wt% of Si, 0.001-5.0 wt% of Sn, 0.1-5.0 wt% of Zn, 0.005-1.0 wt% of Mg, 0.0003-0.005 wt% of S, 0.0003-0.01 wt% of C and the balance of Cu with inevitable impurities, wherein respective contents of Mg and S simultaneously satisfy the following inequalities (1) and (2):

$$0.5[\text{Mg}] + [\text{S}] \geq 0.005 \dots(1)$$

$$0.25[\text{Mg}] \geq [\text{S}] \dots(2),$$

and the alloy has an average crystal grain size in the direction of sheet thickness of 20 μm or less.

[Claim 3] A high strength copper alloy excellent in stamping workability and suitable for silver plating, comprising 0.4-4.0 wt% of Ni, 0.05-1.0 wt% of Si, 0.001-5.0 wt% of Sn, 0.1-5.0 wt% of Zn, 0.005-1.0 wt% of Mg, 0.0003-0.005 wt% of S, 0.0003-0.01 wt% of C, and 0.001-1.0 wt% in total amount of one kind, or two kinds or more of Be, B, Al, P, Ti, V, Cr, Mn, Fe, Co, Pb, Ca, Zr, Nb, Mo, Ag, In, Sb, Hf, and Ta as side component(s), and the balance of Cu with inevitable impurities, wherein respective Mg and S simultaneously satisfy the following inequalities (1) and (2):

$$0.5[\text{Mg}] + [\text{S}] \geq 0.005 \quad \dots (1)$$

$$0.25[\text{Mg}] \geq [\text{S}] \quad \dots (2).$$

[Claim 4] A high strength copper alloy excellent in stamping workability and suitable for silver plating, comprising 0.4-4.0 wt% of Ni, 0.05-1.0 wt% of Si, 0.001-5.0 wt% of Sn, 0.1-5.0 wt% of Zn, 0.005-1.0 wt% of Mg, 0.0003-0.005 wt% of S, 0.0003-0.01 wt% of C, and 0.001-1.0 wt% in total amount of one kind, or two kinds or more of Be, B, Al, P, Ti, V, Cr, Mn, Fe, Co, Pb, Ca, Zr, Nb, Mo, Ag, In, Sb, Hf, and Ta as side component(s), and the balance of Cu with inevitable impurities, wherein respective Mg and S simultaneously satisfy the following

inequalities (1) and (2):

$$0.5[\text{Mg}] + [\text{S}] \geq 0.005 \dots(1)$$

$$0.25[\text{Mg}] \geq [\text{S}] \dots(2),$$

and the alloy has an average crystal grain size in the direction of sheet thickness of 20 μm or less.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention belongs] The present invention relates to a high strength copper alloy excellent in stamping workability and silver plating suitableness, which is used in electric/electronic parts such as a semiconductor lead frame, a terminal, a connector, a relay and a switch.

[0002]

[Prior Art] Cu-Ni-Si-series copper alloys have both strength and electrical conductivity and hence are widely used in electric/electronic parts such as a semiconductor lead frame, a terminal and a connector. In recent years, associated with miniaturization, light-weight and high integration of electric/electronic parts, contraction in lead distance of a lead frame or contraction of inter-electrode pitch of a connector is being attempted. This results in an increasing demand not only for attaining high strength and high electrical conductivity, but also for a material excellent in stamping workability (reduced

burrs and sagging after the stamping working) and causing no wear of a stamping die (see, for example, JP-A-2-66130). In addition, these electric/electronic parts are sometimes subjected to silver plating, and in accordance with increasing demand for improved reliability, silver plating suitability has become increasingly valued than conventionally (see, for example, JP-A-63-130739, 5-59468, and 8-319528).

[0003]

[Problems that the Invention is to Solve] In Cu-Ni-Si-series copper alloys for electric/electronic parts, Mg is used as an additive element for preventing the electrical conductivity from decreasing and for increasing the strength. Then, Mg, as described in JP-A-2-66130, has a great effect on stamping workability and reduction in the wear of a stamping die, however, it is known that Mg deteriorates silver plating suitability (generation of protrusions of silver plating) even with a very small quantity. An object of the present invention is to provide a high strength, Mg-containing Cu-Ni-Si-series copper alloy, reconciling both the stamping workability and silver plating suitability with each other, which properties have been hitherto considered mutually contradictory.

From lines 23 to 30 in column 4 on page (3)

[0014] (C) The present inventors have found that C has the effect of improving the stamping workability of Mg-containing Cu-Ni-Si-series copper alloy. However, if C content is less than 0.0003 wt%, the above effect is small, while if C content is over 0.01 wt%, the above effect is saturated and the hot workability of the alloy is deteriorated. Therefore, the content of C is set to 0.0003 to 0.01 wt%, and preferably 0.001 to 0.01 wt%.
From line 41 in column 4 on page (3), to line 3 in column 5 on page (4)

[0016] (Crystal grain size) The present inventors have found that in Mg-containing Cu-Ni-Si-series copper alloy, in particular, crystal grain size in the direction of sheet thickness is involved in the stamping workability. If the average crystal grain size in the direction of sheet thickness of the alloy in the state of a final sheet product is 20 μm or less, the stamping workability can be improved. Desirably, the average crystal grain size of the alloy is 15 μm or less. Even if the crystal grain size is over 20 μm in the stage of recrystallization, it is included within the above range when the crystal grains become flat during subsequent cold working to give an average crystal grain size in the direction of sheet thickness of 20 μm or less. Further, in the case of a so-called a fiber tissue, which is observed in a material

subjected to cold working with reduction of 90% or more in total after the recrystallization, crystal grains are difficult to observe. However, such a fiber tissue is also encompassed by the present invention.

Concise explanation with respect to JP-A-11-43731

JP-A-11-43731 describes a high strength copper alloy excellent in stamping workability and silver-plate adhesion property. However, the copper alloy in JP-A-11-43731 is applicable only in the use in which stamping workability and silver-plate adhesion property are required. Such an applicable use is different between JP-A-11-43731 and the present invention.

Further, the copper alloy in JP-A-11-43731 differs from the copper alloy of the present invention. That is, in the copper alloy of JP-A-11-43731, 0.0003-0.01 wt% of C is essential, but C is not an essential element in the alloy of the present invention. In JP-A-11-43731, the reason why C of the specific amount is essential is described.

Still further, the copper alloy in JP-A-11-43731 is limited to have a specific average crystal grain size in the direction of sheet thickness of 20 μm or less. This definition in JP-A-11-43731 differs from the definition of the crystal grain diameter in the alloy of the present invention.

In sum, the alloy of the present invention differs from that in JP-A-11-43731, in the points of the use, the constitution (alloy composition), and the definition of alloy's grain size.

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(54) COPPER ALLOY FOR ELCTRICALLY CONDUCTIVE SPRING AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a copper alloy combining excellent mechanical properties, conductivity, stress relaxation characteristics and bending workability.

SOLUTION: This copper alloy is the one having a compsn. contg., as essential components, by weight, 1.0 to 3.5% Ni, 0.2 to 0.9% Si, 0.01 to 0.20% Mg and 0.05 to 1.5% Sn, in which each content of S and O is limited to <0.005%, and the balance Cu with inevitable impurities, and the grain size thereof is regulated to >1 to 25 μm . Thus, this is suitable for terminals, connector materials and switch materials. Furthermore, as for the method for producing it, after cold working, recrystallization treatment is executed at 700 to 920° C.

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CLAIMS

[Claim(s)]

[Claim 1] The copper alloy for conductive springs which Mg is restricted 0.01 - 0.20wt% 0.2 - 0.9wt%, a 0.05-1.5wt% implication, S, and O content are restricted for Sn to less than [0.005wt%], respectively, nickel is consisted of the remainder Cu and an unescapable impurity in 1.0 - 3.5wt% and Si, and the grain size number exceeds 1 micrometer, and is characterized by being 25 micrometers or less as a principal component.

[Claim 2] The copper alloy for conductive springs which Sn is restricted 0.05 - 1.5wt% 0.01 - 0.20wt%, a 0.2-1.5wt% implication, S, and O content are restricted for Zn to less than [0.005wt%], respectively, 1.0 - 3.5wt% and Si are consisted of the remainder Cu and an unescapable impurity in 0.2 - 0.9wt% and Mg, and the grain size number exceeds 1 micrometer, and is characterized for nickel by being 25 micrometers or less as a principal component.

[Claim 3] a copper alloy according to claim 1 or 2 -- further -- 0.005-0.3wt%Ag and 0.01-0.5wt%Mn -- it chooses from 0.005 - 0.2wt% Fe, Cr, 0.05-2.0wt%Co, and 0.005-0.1wt%P, respectively -- having -- one sort or two sorts or more -- a total amount -- 0.005wt(s)% - 2.0wt% -- the copper alloy for conductive springs characterized by containing

[Claim 4] a copper alloy according to claim 1 or 2 -- further -- one sort of 0.005-0.1wt%Pb and 0.005 - 0.03wtBi, or two sorts -- a total amount -- 0.005 - 0.13wt% -- the copper alloy for conductive springs characterized by containing

[Claim 5] To a pan at a copper alloy according to claim 1 or 2 0.005-0.3wt%Ag, It Fe(s), 0.01-0.5wt%Mn -- respectively -- 0.005 - 0.2wt% -- It is chosen from Cr, 0.05-2.0wt%Co, and 0.005-0.1wt%P. One sort or two sorts or more, and one sort of 0.005-0.1wt%Pb and 0.005 - 0.03wtBi, or two sorts -- a total amount -- 0.005wt(s)% - 2.0wt% -- the copper alloy for conductive springs characterized by containing

[Claim 6] The copper alloy for conductive springs according to claim 1 to 5 characterized by being what used for a terminal, connector material, or switch material.

[Claim 7] The manufacture method of the copper alloy for conductive springs according to claim 1 to 6 characterized by performing recrystallization processing at 700-920 degrees C after cold working.

[Claim 8] The manufacture method of the copper alloy for conductive springs according to claim 1 to 6 characterized by performing an aging treatment at 420-550 degrees C after performing recrystallization processing at 700-920 degrees C after cold working.

[Claim 9] The manufacture method of the copper alloy for conductive springs according to claim 1 to 6 characterized by performing an aging treatment at 420-550 degrees C after performing recrystallization processing at 700-920 degrees C after cold working and performing 25 more% or less of cold working.

[Claim 10] The manufacture method of the copper alloy for conductive springs according to claim 1 to 6 characterized by performing 25 more% or less of cold working, and low temperature annealing after performing recrystallization processing at 700-920 degrees C after cold working and performing 25% or less of cold working, and a 420-550-degree C aging treatment next.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] Especially this invention relates to the copper alloy for conductive springs suitable for a terminal and connector material, switch material, etc., and its manufacture method about the copper alloy for conductive springs, and its manufacture method.

[0002]

[Description of the Prior Art] A copper alloy is conventionally used as a terminal and a charge of connector material, and many Cu-Zn system alloys, Cu-Fe system alloys excellent in thermal resistance, and Cu-Sn system alloys are used. Although many cheap Cu-Zn system alloys are especially used for the use of an automobile etc., it is the present condition that it is becoming impossible, as for the terminal for automobiles in recent years and a connector, for a Cu-Fe system alloy and an Cu-Sn system alloy to also correspond of course with a Cu-Zn system alloy since a miniaturization inclination is remarkable and it is exposed to the harsh environments in an engine room etc. in many cases.

[0003] Thus, the property for which a terminal and the charge of connector material are asked is also becoming severer with change of the environment currently used. Although a stress relaxation characteristic, a mechanical strength, thermal conductivity, bending nature, thermal resistance, the connection reliability of Sn plating, the migration property, etc. are variably crossed to the copper alloy used for such a use, it is a property with especially important a mechanical strength, a stress relaxation characteristic, the conductivity of heat and the electrical and electric equipment, and bending nature.

[0004] As a copper system material which fills such severe demand characteristics, the Cu-nickel-Si system alloy attracts attention, for example, JP.61-127842.A is known. However, it has lapsed into the state where such an Cu-nickel-Si system alloy cannot bear use, either. Specifically, when the tab width of face of the male terminal inserted in the miniaturization of parts, for example, a common core-box terminal, is miniaturized from 090 terminals which are about 2mm to 040 terminals which are about 1mm, the width of face of the spring section is about 1mm, and if parts are miniaturized in this way, it is difficult to obtain sufficient connection resilience. Moreover, although many devices are made by the structure of a terminal in order to secure the connection resilience in the spring section in relation to a miniaturization consequently, it is severer, and in conventional Cu-nickel-Si, the bending nature required of material is also bent and a crack produces it in many cases in the section. The same is said of a stress relaxation characteristic, and prolonged use is an impossible situation with the conventional Cu-nickel-Si system alloy by the increase of stress by which a load is carried out to material, and elevated-temperature-ization of an operating environment.

[0005] In order to improve a stress relaxation characteristic under such a situation, addition of Mg is effective, for example, the effectiveness of Mg is shown in JP.61-250134.A, JP.5-59468.A, etc. However, although a stress relaxation characteristic improves by Mg addition, the improvement of bending nature is indispensable for bending nature to deteriorate, to be unable to bear 180-degree adhesion bending, and to use it for an automobile connector etc. Moreover, although examination for improving bending nature was also carried out, since this was a strong low material, it was that from which a desired property is not acquired. Furthermore, if the conductivity of heat and the electrical and electric equipment is bad, in order that a stress relaxation characteristic may promote stress relaxation by self generation of heat as it is good, the balance of conductivity and a stress relaxation characteristic is important.

[0006]

[Problem(s) to be Solved by the Invention] Although the copper system material which examines bending nature, a stress relaxation characteristic, etc. and fills severe demand characteristics is proposed as mentioned above, this invention is a copper alloy which combines the outstanding mechanical property, conductivity, a stress relaxation characteristic, and bending nature, and offers the suitable copper alloy for a terminal and a connector.

[0007]

[Means for Solving the Problem] It is the copper alloy for conductive springs which this invention solves the above-mentioned technical problem, and Mg is restricted 0.01 - 0.20wt% 0.2 - 0.9wt%, a 0.05-1.5wt% implication, S, and O content are restricted for Sn to less than [0.005wt%], respectively, nickel is consisted of the remainder Cu and an unescapable impurity in 1.0 - 3.5wt% and Si, and the grain size number exceeds 1 micrometer, and is characterized by being 25 micrometers or less as a principal component. Moreover, in the above-mentioned composition, it is the range which does not have a bad influence on the property of this invention, and even if it adds other alloying elements, for example, less than 0.2% of Zn, it does not interfere. Moreover, this invention is a copper alloy for conductive springs which Sn is restricted 0.05 - 1.5wt% 0.01 - 0.20wt%, a 0.2-1.5wt% implication, S, and O content are restricted for Zn to less than [0.005wt%], respectively, 1.0 - 3.5wt% and Si are consisted of the remainder Cu and an unescapable impurity in 0.2 - 0.9wt% and Mg, and the grain size number exceeds 1 micrometer, and is characterized for nickel by being 25 micrometers or less as a principal component.

[0008] moreover, this invention is further chosen as the above-mentioned copper alloy from Ag, Mn, Fe, Cr, Co, and P -- having -- one sort or two sorts or more -- a total amount -- 0.005wt(s)% - 2.0wt% -- it is the copper alloy characterized by containing For nickel Si 1.0 - 3.5wt% as a principal component specifically 0.2 - 0.9wt%, For Mg Sn 0.01 - 0.20wt% A 0.05-1.5wt% implication, Further 0.005-0.3wt%Ag, 0.01-0.5wt%Mn, Respectively 0.005 - 0.2wt% Fe, Cr, 0.05-2.0wt%Co, It is chosen from 0.005-0.1wt%P, one sort or two sorts or more in a total amount A 0.005wt%-2.0wt% implication, It is the copper alloy for conductive springs which S and O content are restricted to less than [0.005wt%], respectively, it consists of the remainder Cu

and an unescapable impurity, and the grain size number exceeds 1 micrometer, and is characterized by being 25 micrometers or less. For nickel Si 1.0 - 3.5wt% as a principal component Moreover, 0.2 - 0.9wt%, For Mg Sn 0.01 - 0.20wt% 0.05 - 1.5wt%, Zn to a 0.2-1.5wt% implication and a pan 0.005-0.3wt%Ag, It Fe(s). 0.01-0.5wt%Mn -- respectively -- 0.005 - 0.2wt% -- It is chosen from Cr, 0.05-2.0wt%Co, and 0.005-0.1wt%P. one sort or two sorts or more in a total amount A 0.005wt%-2.0wt% implication, It is the copper alloy for conductive springs which S and O content are restricted to less than [0.005wt%], respectively, it consists of the remainder Cu and an unescapable impurity, and the grain size number exceeds 1 micrometer, and is characterized by being 25 micrometers or less.

[0009] moreover, the copper alloy of the above [this invention] -- further -- one sort of Pb and Bi, or two sorts -- a total amount -- 0.005 - 0.13wt% -- it is the copper alloy characterized by containing For nickel Si 1.0 - 3.5wt% as a principal component specifically 0.2 - 0.9wt%, For Mg Sn 0.01 - 0.20wt% A 0.05-1.5wt% implication, One sort of further 0.005-0.1wt%Pb and 0.005 - 0.03wt%Bi, or two sorts in a total amount A 0.005-0.13wt% implication, It is the copper alloy for conductive springs which S and O content are restricted to less than [0.005wt%], respectively, it consists of the remainder Cu and an unescapable impurity, and the grain size number exceeds 1 micrometer, and is characterized by being 25 micrometers or less. For nickel Si 1.0 - 3.5wt% as a principal component Moreover, 0.2 - 0.9wt%, For Mg Sn 0.01 - 0.20wt% 0.05 - 1.5wt%, Zn to a 0.2-1.5wt% implication and a pan 0.005-0.1wt%Pb. One sort of 0.005 - 0.03wt%Bi, or two sorts in a total amount A 0.005-0.13wt% implication, It is the copper alloy for conductive springs which S and O content are restricted to less than [0.005wt%], respectively, it consists of the remainder Cu and an unescapable impurity, and the grain size number exceeds 1 micrometer, and is characterized by being 25 micrometers or less.

[0010] moreover, it is further chosen as the above-mentioned copper alloy from Ag, Mn, Fe, Cr, Co, and P -- having -- one sort or two sorts or more and one sort of Pb and Bi, or two sorts -- a total amount -- 0.005wt(s)% - 2.0wt% -- it is the copper alloy characterized by containing For nickel Si 1.0 - 3.5wt% as a principal component specifically 0.2 - 0.9wt%, For Mg Sn 0.01 - 0.20wt% A 0.05-1.5wt% implication, Further 0.005-0.3wt%Ag, 0.01-0.5wt%Mn, Respectively 0.005 - 0.2wt% Fe, Cr, 0.05-2.0wt%Co, It is chosen from 0.005-0.1wt%P. One sort or two sorts or more, and 0.005-0.1wt%Pb, One sort of 0.005 - 0.03wt%Bi, or two sorts in a total amount A 0.005wt%-2.0wt% implication, It is the copper alloy for conductive springs which S and O content are restricted to less than [0.005wt%], respectively, it consists of the remainder Cu and an unescapable impurity, and the grain size number exceeds 1 micrometer, and is characterized by being 25 micrometers or less. For nickel Si 1.0 - 3.5wt% as a principal component Moreover, 0.2 - 0.9wt%, For Mg Sn 0.01 - 0.20wt% 0.05 - 1.5wt%, Zn to a 0.2-1.5wt% implication and a pan 0.005-0.3wt%Ag, It Fe(s). 0.01-0.5wt%Mn -- respectively -- 0.005 - 0.2wt% -- It is chosen from Cr, 0.05-2.0wt%Co, and 0.005-0.1wt%P. One sort or two sorts or more, One sort of 0.005-0.1wt%Pb and 0.005 - 0.03wt%Bi, or two sorts in a total amount And a 0.005wt%-2.0wt% implication, It is the copper alloy for conductive springs which S and O content are restricted to less than [0.005wt%], respectively, it consists of the remainder Cu and an unescapable impurity, and the grain size number exceeds 1 micrometer, and is characterized by being 25 micrometers or less.

[0011] Moreover, the above-mentioned copper alloy of this invention is characterized by being what is used for a terminal, connector material, or switch material. Moreover, this invention is the manufacture method of the copper alloy for conductive springs characterized by performing recrystallization processing at 700-920 degrees C after cold working. Moreover, after [which is the manufacture method of the copper alloy for conductive springs characterized by performing an aging treatment at 420-550 degrees C] performing recrystallization processing at 700-920 degrees C after cold working, performing recrystallization processing at 700-920 degrees C after cold working and performing 25 more% or less of cold working again, it is the manufacture method of the copper alloy for conductive springs characterized by performing an aging treatment at 420-550 degrees C. Furthermore, after performing recrystallization processing at 700-920 degrees C after cold working and performing 25% or less of cold working, and a 420-550-degree C aging treatment next, it is the manufacture method of 25 more% or less of cold working, and the copper alloy for conductive springs characterized by performing low temperature annealing.

[0012]

[Function] The copper alloy of this invention makes it the main point to carry out the amount addition of specification of Sn, Mg, and the Zn, and to restrict S and O content to the copper alloy which the compound of nickel and Si is deposited in Cu matrix, and has a suitable mechanical strength, and heat and electric conductivity, and to exceed 1 micrometer for a grain size number to it, and to improve a stress relaxation characteristic and bending nature as 25 micrometers or less. This invention persons find out that the material which has the property which was excellent as the copper alloy for conductive springs which has the property which was excellent in specifying the content of this copper alloy component in detail practical especially a terminal, and an object for connectors can be made to realize, and, as a result, get the copper alloy of this invention.

[0013] The reason for component limitation of the copper alloy of this invention is explained below. If Cu is made to contain nickel and Si, an nickel-Si compound will be made, this is deposited in Cu, and intensity and conductivity are raised. There are few amounts of deposits and target intensity [be / less than / 1.0wt% / the amount of nickel] is not obtained. Conversely, when the amount of nickel exceeds 3.5wt(s)%, it will have a bad influence also on about [that the intensity which casting and the deposit which does not contribute to an on-the-strength rise at the time of hot working arise and balances a content cannot be obtained], hot-working nature, and bending nature. Since the amount of Si is considered that the compound of nickel and Si which deposits is a nickel₂Si phase, if the amount of nickel is determined, optimal Si content will be decided. Sufficient intensity cannot be obtained like the time with few amounts of nickel as the amount of Si is less than [0.2wt%]. Conversely, when Si content exceeds 0.9wt(s)%, the same problem as the case where there are many amounts of nickel arises. Preferably, it is desirable to adjust nickel and to adjust Si to 0.4 - 0.7wt% 1.7 - 2.8wt%.

[0014] Mg and Sn are important alloying elements which constitute the copper alloy of this invention. There are these elements with regards to mutual, and they have realized good property balance. Next, the reason for limitation of these elements is explained. Although Mg improves a stress relaxation characteristic sharply, it has a bad influence on bending nature. From a viewpoint of a stress relaxation characteristic, many contents are so good that there are at more than 0.01wt%. Conversely, if a content exceeds 0.20wt(s)% from a viewpoint of bending nature, it is difficult to obtain good bending nature. From such a viewpoint, the content range of Mg shows good balance in 0.01 - 0.20wt%. The more desirable content range of Mg is 0.01 - 0.1wt% from a viewpoint of bending nature.

[0015] Furthermore, it found out that a stress relaxation characteristic was more improvable, maintaining good bending nature by adding Sn. Although Sn has the improvement effect of a stress relaxation characteristic and the effect is not so large as Mg, it is with regards to Mg and mutual, and good property balance is shown. If Sn is contained exceeding 1.5wt(s)%, the conductivity of heat and the electrical and electric equipment will deteriorate, and a problem will be caused practically. Although Sn content

also has balance with the amount of Mg, 0.05 - 1.5wt% shows good property balance. Specifically, when Mg is 0.01 - 0.05wt%, 0.8 - 1.5wt% of Sn is desirable, and when the amount of Mg is 0.05 - 0.1wt%, 0.05 - 0.8wt% of Sn is desirable.

[0016] Bending nature is improvable although Zn does not contribute to a stress relaxation characteristic. Zn -- 0.2 - 1.5wt% -- desirable -- 0.3 - 1.0wt% -- by containing, even if it makes Mg contain to a maximum of 0.20 wt(s)%, it is satisfactory practically -- the bending nature of level can be attained moreover, the operation which Zn has the effect of improving the heat-resistant detachability of Sn plating or pewter plating, and a migration property, and improves punching processability -- having -- a practical viewpoint to Zn -- 0.2wt(s)% -- desirable -- more than 0.3wt% -- it is desirable to make it contain Although hot-working nature will be checked if Pb and Bi are added so much as an element which improves punching processability, although there are Pb and Bi, since Zn can improve punching processability, without having a bad influence on manufacturability, it is an effective alloying element. the upper limit -- the conductivity of heat and the electrical and electric equipment -- taking into consideration -- 1.5wt% -- it is 1.0wt(s)% preferably In addition, it is shown that it is in the better inclination at **** with Mg also from this example.

[0017] As mentioned above, although the reason which limited the addition range of Mg, Sn, and Zn was explained in full detail, it is limited within the limits of these elements, and considering as the maximum content, respectively is not desirable. The range of a content with the practically best balance is Zn:0.3 - 0.8wt% Sn:0.2 - 0.5wt% Mg:0.05 - 0.15wt%.

[0018] Next, the reason which limited the range of the content of Ag, Mn, Fe, Cr, Co, and P is explained. in that processability is improved, Ag, Mn, Fe, Cr, Co, and P have the analogous function, and choose it from Ag, Mn, Fe, Cr, Co, and P -- having -- one sort or two sorts or more -- 0.005wt(s)% - 2.0wt% -- it is made to contain

[0019] While Ag raises thermal resistance and raises intensity, it can prevent big and rough-ization of crystal grain, and can improve bending nature. Although adding the third various element was the place tried conventionally in order to raise the intensity of an Cu-nickel-Si system alloy, they were those in which conductivity is lowered sharply, or a bending moldability deteriorates, and the property which is not desirable as a use for electronic equipment appears. this invention finds out that Ag is effective, as a result of repeating examination of the element which improves intensity and does not have a bad influence on other properties. a content is less than [0.005wt%] -- the effect -- not appearing -- reverse -- 0.3wt(s)% -- since it exceeds, and no bad influence on a property will serve as cost quantity although there is if contained, the optimal content of Ag is 0.005 - 0.3wt%, and is 0.005 - 0.1wt% more preferably

[0020] Mn is effective in improving hot-working nature at the same time it raises intensity, and the effect corresponding to the content is not not only acquired, but [even if the effect is small in it being less than / 0.01wt% / and being contained exceeding 0.5wt%,] it degrades conductivity. Therefore, the optimal content range of Mn is 0.01 - 0.5wt%, and is 0.03 - 0.3wt% more preferably.

[0021] Fe and Cr combine with Si, form an Fe-Si compound and an Cr-Si compound, and raise intensity. Moreover, the trap of the Si which remains in a copper matrix, without forming a compound with nickel is carried out, and it is effective in improving conductivity. Since an Fe-Si compound and an Cr-Si compound have low precipitation-hardening ability, it is not a best policy to make many compounds generate. Moreover, if contained exceeding 0.2wt%, bending nature will deteriorate. The addition in the case of containing Fe and Cr from these viewpoints is 0.005 - 0.2wt%, and is 0.005 - 0.1wt% more preferably.

[0022] Co forms Si and a compound like nickel and raises a mechanical strength. Since it is expensive, although it compared Co with nickel, and it uses the Cu-nickel-Si system alloy in this invention, as long as it is allowed in cost, it may choose an Cu-Co-Si system and an Cu-nickel-Co-Si system. When an Cu-Co-Si system carries out an aging deposit, a mechanical strength and conductivity become good slightly from an Cu-nickel-Si system. Therefore, it is effective in the member ***** (ed) in the conductivity of heat and the electrical and electric equipment. Moreover, since it is slightly high, as for an Co-Si compound, a stress relaxation characteristic also tends to be improved for precipitation-hardening ability a little. The optimal addition in the case of adding Co from these viewpoints is 0.05 - 2.0wt%.

[0023] P has the effect of improving conductivity at the same time it raises intensity. A lot of content promotes a grain-boundary deposit, and reduces bending nature. Therefore, the optimal content range in the case of adding P is 0.005 - 0.1wt%, and is 0.005 - 0.05wt% more preferably. Although what is necessary is just to have determined suitably according to the property searched for when two or more sorts of these were added simultaneously, it could be 0.005 - 2.0wt% in the total amount from viewpoints, such as thermal resistance, Sn plating, pewter plating heatproof detachability, and conductivity.

[0024] Next, the reason which limited the range of the content of Pb and Bi is explained. that to which Pb and Bi improve punching processability -- it is -- one sort of Pb and Bi, or two sorts -- 0.005 - 0.13wt% -- it contains Pb is an alloying element which improves punching processability. The charge of terminal material is asked for the more excellent processability with press improvement in the speed in recent years. It distributes in a copper matrix, and since Pb becomes the origin of destruction, it improves punching processability. When there is no property improvement effect that the amount of Pb(s) is less than [0.005wt%] and it adds exceeding 0.1wt%, in order to also degrade bending nature, 0.005 - 0.1wt% is the optimal and it not only reduces hot-working nature, but it is 0.005 - 0.05wt% more preferably. It is the alloying element which also pierces Bi and improves processability. 0. If the property improvement effect is small in it being less than [0.005wt%] and it adds exceeding 0.03wt%, the same property fall as Pb will be caused. Therefore, the optimal content range of Bi is 0.005 - 0.03wt%, and is 0.005 - 0.02wt% more preferably.

[0025] Although what is necessary is just to have determined suitably according to the property which is chosen from these [Ag, Mn, Fe, Cr, Co, and P], and is searched for one sort or two sorts or more and one sort of Pb and Bi, or when it contains two sorts simultaneously, it could be 0.005 - 2.0wt% in the total amount from viewpoints, such as thermal resistance, Sn plating, pewter plating heatproof detachability, and conductivity.

[0026] Next, the reason for having restricted S and O content to less than [0.005wt%] is explained. Usually, into a industrial copper material, S and O2 grade aims at realization of the property which was excellent in ***** rare ** conjointly with the convention of the grain size number to which this invention mentions these contents later with the alloy content mentioned above with restricting strictly. S is an element which worsens hot-working nature, is specifying the content as less than [0.005wt%], and raises hot-working nature. It is desirable to make especially S content into less than [0.002wt%]. Mg oxidizes that the content is more than 0.005wt%, and, as for O, bending nature deteriorates. It is desirable less than [0.005wt%] and to make O content into less than [0.002wt%] especially. Although contained in many cases in the usual copper system material at the minute amount, S and O which were explained above were important especially in the copper alloy of this invention, and the property excellent in specifying the content is acquired, and they found out realizing the suitable property for a terminal and the charge of connector material.

[0027] In the composition of the copper alloy of this invention mentioned above, in order to realize the property suitably, it is required for a grain size number to exceed 1 micrometer and to set to 25 micrometers or less. In a recrystallized structure, it is easy to change with a mixed grain size that a grain size number is 1 micrometer or less, and a stress relaxation characteristic declines at the same time bending nature falls. Conversely, even if a grain size number grows exceeding 25 micrometers, it has a bad influence on bending nature. Therefore, a grain size number needs to exceed 1 micrometer and needs to adjust it to 25 micrometers or less.

[0028] Subsequently, the manufacturing method of the copper alloy of this invention is explained. Cold working, for example, after cold-rolling, the copper alloy of this invention heat-treats the making it solution-ize with recrystallization purpose, and quenches immediately. Moreover, an aging treatment is performed if needed. In order to exceed 1 micrometer and to adjust the grain size number in the copper alloy of this invention to the range of 25 micrometers or less, it is necessary to control the conditions of recrystallization processing in detail. Heat treatment at the temperature of less than 700 degrees C tends to serve as a mixed grain size, and in the temperature exceeding 920 degrees C, since crystal grain tends to grow big and rough, it performs recrystallization processing at 700-920 degrees C after cold working. Moreover, a cooling rate is quick as much as possible, and it is desirable to cool at 10 degrees C/s or more in speed.

[0029] Next, about the conditions of aging heat treatment, the amount of precipitation hardening is inadequate in aging temperature being less than 420 degrees C, and sufficient property cannot be pulled out. Conversely, if it processes at the temperature exceeding 550 degrees C, a deposit phase will grow big and rough and not only intensity falls, but it will reduce a stress relaxation characteristic. Therefore, aging-treatment temperature was made into 420-550 degrees C. Furthermore, it turns out that a stress relaxation characteristic receives influence in the state of a deposit phase greatly, and they are the best conditions near [where aging intensity shows a peak] the temperature. On the other hand, as for bending nature, it is desirable for aging intensity to heat-treat by the overaging side a little from the temperature which shows a peak. Processing at 460-530 degrees C is preferably the optimal from such a viewpoint.

[0030] Moreover, after performing recrystallization processing (solution-izing) at 700-920 degrees C after cold working and performing cold working (25% or less) further, an aging treatment is performed at 420-550 degrees C. Although the aging treatment was immediately performed after solution-izing in the example described later, it is also effective between solution-izing and aging to perform cold working. In this case, processing of 25% or less of reduction of area which does not degrade bending nature is desirable. Moreover, after performing recrystallization processing (solution-izing) at 700-920 degrees C after cold working and performing an aging treatment at cold working (25% or less) and 420-550 degrees C, 25 more% or less of cold working and low temperature annealing are performed. Thus, you may perform cold working after an aging treatment. In this case, in order not to degrade the bending nature which is the feature of this invention, processing of 25% or less of reduction of area is desirable. Furthermore, when performing cold working after the above-mentioned aging treatment, performing annealing at low temperature comparatively after that is recommended. In performing this annealing by batch-type annealing, when annealing between 0.5-5hr and ** performs at the temperature of 250-400 degrees C, it is desirable to carry out on conditions (5-60s) with the temperature of 600-800 degrees C. This annealing carries out the rearrangement of the transposition introduced by cold working, and has the operation which suppresses movement of transposition as a result. Therefore, when the above-mentioned cold working is performed, a stress relaxation characteristic can be improved by annealing. You may correct a tension leveler, roller BERA, etc. before the last heat treatment or to the back if needed.

[0031]

[Embodiments of the Invention] The copper alloy of this invention has the outstanding mechanical strength, bending nature, a stress relaxation characteristic, Sn plating detachability, punching nature, etc., is equipped with the property for which general electrical conducting materials, such as a terminal and connector material, switch material, and relay material, etc. are asked especially, and explains it in detail according to an example.

[0032]

[Example 1] The 1st example of this invention is shown in Tables 1-6, and it explains. Alloy composition of the example of this invention, Table 2, and Table 3 are alloy composition of the example of comparison, and the conventional example, and, in the property of the example alloy of this invention, Table 5, and Table 6, Table 4 shows [Table 1] the property of the alloy of the example of comparison, and the conventional example. In addition, the arrow of front Naka shows the same thing as the upper column, and the proof stress value of (*) is low, and since it caused plastic deformation in the sample set stage, it carries out a test stop.

[0033] First, with the RF fusion furnace, the alloy of the composition described in Table 1 - 3 was dissolved, and it cast with the cooling rate of 6 degrees C/s. The size of an ingot is 150mm in the thickness of 30mm, width of face of 100mm, and length. Next, since these ingots were hot-rolled at 900 degrees C, it cooled promptly. In order to remove a surface oxide film, after carrying out facing to 9mm in thickness, 0.25mm in thickness was processed with cold rolling. Then, the making a test specimen solution-ize with recrystallization purpose, heat treatment for 30s was performed at 750 degrees C, and it quenched with the cooling rate of 15 degrees C/s or more immediately. The aging treatment performed heat treatment of 515 degree-Cx 2 hours in the inert atmosphere, and was taken as the material with which an examination is presented.

[0034] It sampled from the manufactured material, the grain size number was measured, and various characterization of fracture surface (%) and a ratio, and a barricade (micrometer) was performed as TS(tensile strength)N/mm², El(elongation) %, EC (conductivity) %IACS, bending nature, S.R.R(rate of stress relaxation) %, Sn plating detachability, and punching nature.

[0035] The grain size number, i.e., the size of crystal grain, observed by using a comparison method and an intercept method together according to JISH0501. In the comparison method, microscope observation (75 times or 200 times) was carried out, and the test piece was measured. At the intercept method, it measured in the board thickness cross section parallel to the processing direction. Tensile strength is JISZ2241 and measured conductivity as a value which shows the conductivity of heat and the electrical and electric equipment according to JISH0505.

[0036] As for evaluation of bending nature, the inside bend radius performed 180-degree adhesion bending of OR. the index of evaluation -- A. wrinkling -- there is nothing -- fitness B. -- C. by which a small wrinkling is observed -- D. which has not resulted in the crack although a big wrinkling is observed -- E. by which a detailed crack is observed -- it evaluated in observing [a crack]-clearly 5 stage, and more than the evaluation C was judged to be the level which is satisfactory practically

[0037] Evaluation of a stress relaxation characteristic was performed based on EMAS-3003 which are the JEOL material Semiconductor Equipment & Materials International standard. The ***** block formula was adopted here, load stress was set

up so that 450Ns /of surface maximum stress might be set to 2 mm, and it examined by the 150-degree C thermostat. The rate of relief after 1000hr examinations (S. R.R) showed to Table 4 - 6.

[0038] The ***** block sequence of the test method of stress relaxation is shown in drawing 1 (a), (b), and (c). It is a perspective diagram and (b) is a side elevation, and drawing 1 (a) supports one side of a sample (1) by the attachment component (3) to a pedestal (2) at support-at-one-end ***** and changes another side into the state where it was distorted to the sample (1) with a block (4), and deltao (initial deflection variation rate) was given. Predetermined-time (this example 1000 hr(s)) heating of the sample (1) is carried out in this state at 150 degrees C. As shown in the side elevation of drawing 1 (c) after predetermined-time progress, distortion deltat (permanent deflection variation rate) in the state where the block (4) was removed was measured, and it asked for the rate of stress relaxation (%) by the following formula.

rate (%) of stress relaxation = (deltat/deltao) x100 -- in addition -- initial deflection -- a variation rate is calculated from Young's modulus, board thickness, etc. so that surface maximum stress may become a predetermined value (450N/mm2) (the calculation method is based on EMAS-3003)

[0039] The heating detachability of Sn plating evaluated plating ablation of the portion by viewing, after carrying out air heating of 150 degree-Cx 1000 hours for the test piece which gave 1-micrometer gloss Sn plating, and it carried out 180 adhesion bending and bend return. When ablation of solder was accepted, it was described in Tables 4-6 as "**."

[0040] Punching nature was investigated by examining by piercing with metal mold (product made from SKD11) (a 1mmx5mm square hole being prepared). And the punching side of the sample extracted from a part for the 5001st time to the 10000th punching at random 20 pieces was observed, and the thickness of the fracture section was measured. The average of the rate of the thickness of the fracture section to the thickness of a test piece is shown in Tables 4-6 by % display (it is displayed as F.A.R in front Naka). The height of the barricade of the sample similarly extracted from the 5001st time to the 10000th punching portion at random 20 pieces was found with the contact process configuration measurement machine also about barricade measurement, and the average was indicated to the table.

[Table 1]

[Table 2]

	No	Ni	Si	Mg	Sn	Zn	S	O	その他	結晶粒度
比較例	22	0.8	0.18	0.08	0.34	0.50	0.002	0.001		5
	23	3.8	0.95	0.08	0.33	0.49	0.002	0.001		↑
	24	2.0	0.47	0.003	0.33	0.49	0.002	0.001		↑
	25	2.0	0.48	0.002	0.99	0.50	0.002	0.001		↑
	26	1.9	0.47	0.25	0.33	1.25	0.002	0.001		↑
	27	2.0	0.48	0.08	0.002	0.50	0.002	0.001		↑
	28	2.0	0.48	0.08	2.04	0.50	0.002	0.001		↑
	29	2.1	0.47	0.08	0.31	5.09	0.002	0.001		↑
	30	2.0	0.47	0.07	0.33	0.49	0.002	0.001	Fe0.35	↑
	31	1.9	0.48	0.08	0.32	0.48	0.002	0.001	Pb0.25	↑
	32	1.9	0.46	0.09	0.33	0.49	0.011	0.001		↑
	33	2.0	0.48	0.08	0.32	0.50	0.002	0.007		↑
	34	2.0	0.47	0.08	0.31	0.50	0.002	0.001		≤1
	35	2.0	0.48	0.08	0.32	0.49	0.002	0.001		30

[Table 3]

	No	Ni	Si	Mg	Sn	Zn	S	O	その他	結晶粒度
比較例	36	2.0	0.47	0.07	0.002	0.49	0.002	0.001	Cr0.10	5
	37	1.9	0.48	0.08	0.001	0.48	0.002	0.001	Mn0.39	↑
	38	2.0	0.48	0.08	0.002	0.50	0.002	0.001	B0.008	↑
	39	2.0	0.47	0.08	0.001	0.50	0.002	0.001	Al0.50	↑
	40	2.0	0.48	0.08	0.001	0.50	0.002	0.001	Ti0.10	↑
	41	2.0	0.48	0.08	0.002	0.49	0.002	0.001	In0.10	↑
従来例	42	2.5	0.60	—	—	—	—	—		
	43	1.9	0.50	—	0.4	0.9	—	—		
	44	2.7	0.65	0.17	—	—	—	—		

[Table 4]

	No	TS N/mm ²	EI %	EC %IACS	曲げ 加工性	S. R. R %	Snメッキ 剥離性	打ち抜き性	
								F. A. R(%)	バリ(μm)
本 発 明 例	1	610	16	39	B	22	剥離無し	42	9
	2	670	16	39	B	18	↑	45	6
	3	680	15	38	B	17	↑	46	6
	4	680	14	38	C	17	↑	50	5
	5	660	16	40	B	22	↑	44	7
	6	680	16	33	B	18	↑	46	7
	7	680	15	32	B	14	↑	47	8
	8	670	16	38	C	14	↑	47	6
	9	670	16	36	B	14	↑	51	4
	10	670	16	37	B	18	↑	50	4
	11	680	15	33	C	18	↑	41	10
	12	680	16	31	B	14	↑	54	3
	13	710	15	42	B	15	↑	49	4
	14	700	16	40	B	16	↑	47	4
	15	680	16	39	B	18	↑	45	7
	16	670	16	39	B	19	↑	55	2
	17	660	15	41	B	19	↑	45	8
	18	680	14	39	C	20	↑	46	6
	19	670	16	39	B	18	↑	44	7
	20	670	16	39	B	18	↑	41	9
	21	660	13	39	C	19	↑	39	11

[Table 5]

	No	TS N/mm ²	EI %	EC %IACS	曲げ 加工性	S. R. R %	Snメッキ 剥離性	打ち抜き性	
								F. A. R(%)	バリ(μm)
比 較 例	22	480	19	51	A	—(*)	剥離無し	31	19
	23	680	14	38	D	17	↑	49	4
	24	670	16	40	B	33	↑	40	11
	25	680	16	32	B	31	↑	42	11
	26	670	15	34	D	13	↑	58	2
	27	670	16	42	B	24	↑	45	5
	28	690	15	23	B	13	↑	46	6
	29	680	17	29	B	18	↑	56	2
	30	530	18	43	D	—(*)	↑	37	17
	31	熱間加工中に割れが生じたため製造中止							
	32	熱間加工中に割れが生じたため製造中止							
	33	670	10	40	D	23	剥離無し	46	6
	34	680	12	39	D	22	↑	45	8
	35	650	9	39	D	25	↑	40	12

[Table 6]

	No	TS N/mm ²	EI %	EC %IACS	曲げ 加工性	S. R. R %	Snメッキ 剥離性	打ち抜き性	
								F. A. R (%)	バネ (μm)
比較例	36	650	17	42	B	24	剥離無し	44	8
	37	670	15	35	B	25	↑	46	7
	38	670	16	40	B	25	↑	41	11
	39	670	16	35	B	23	↑	47	8
	40	660	15	40	B	26	↑	46	9
	41	680	16	39	B	24	↑	44	10
従来例	42	670	17	46	B	34	剥離有り	38	13
	43	650	16	38	B	33	剥離無し	37	13
	44	680	11	44	D	19	剥離有り	40	11

[0041] It turns out that the examples 1-21 of this invention show the property which was excellent in all of the various properties of TS (tensile strength), EI (elongation), EC (conductivity), bending nature, S.R.R (rate of stress relaxation), Sn plating detachability, and punching nature so that clearly from Table 4.

[0042] On the other hand, the target intensity is not obtained but punching processability is also inferior in example No. of comparison 22 with few amounts of nickel-Si as compared with other materials. Conversely, although there was no difference in respect of intensity as compared with example No. of this invention 4 with little example No. of comparison 23 in the amount of nickel-Si with many amounts of nickel-Si, bending nature showed the degradation inclination. That is, since bending nature is inferior, it is unsuitable as a terminal and an object for connectors to add nickel-Si more than the amount specified by this invention.

[0043] Example No. of comparison 24 with few additions of Mg are sharply inferior in the stress relaxation characteristic as compared with No. 2 of the example of this invention, and No. 5. Example No. of comparison 25 are inferior to example No. of this invention 6, and No. 7 by the same reason as this. even if this adds Sn independently into the conventional Cu-nickel-Si alloy (conventional example No. 42), it shows that the big improvement effect is not expectable in a stress relaxation characteristic, and is in agreement in the property of the conventional Cu-nickel-Si alloy containing Sn (conventional example No. 43)

[0044] As for example No. of comparison 26 whose addition of Mg is more than the amount of conventions of this invention, bending nature has deteriorated. This is unsuitable as a terminal and connector material. Zn which can improve bending nature a little — more than 1wt% — even if it added, good bending nature was not securable Example No. of comparison 27 with few additions of Sn are inferior in respect of the stress relaxation characteristic as compared with No. 2 of the example of this invention. Conversely, example No. of comparison 28 with many additions of Sn were one of the composition which showed the stress relaxation characteristic which was most excellent in in having performed the effect of Mg, a phase ball, and this time manufacture. However, conductivity becomes the lowest and it cannot be said that it excels in balance. Conductivity becomes low and example No. of comparison 29 with many additions of Zn are not excellent in property balance.

[0045] The Fe-Si compound generated so much example No. of comparison 30 whose addition of Fe is more than the amount of conventions, and the amount of precipitation hardening not only fell, but they had the bad influence on bending nature. Example No. of comparison 31 which made [many] the addition of Pb produced the crack during hot working, and were not able to manufacture it normally. In addition, the crack arose at the time of hot working, and example No. of comparison 32 which have S out of this invention range were not able to perform subsequent characterization. Moreover, the oxide of Mg was generating [O] many example No. of comparison 33, and bending nature deteriorated.

[0046] Example No. of comparison 34 performed annealing for making it recrystallize in 680 degree-Cx30s. Consequently, average crystal grain is 1 micrometer or less, and became the organization where comparatively big crystal grain and small crystal grain are intermingled. Depending on the place which extracts the test piece which performs bending nature, a result which produces a crack was brought for the uneven organization. On the contrary, since example No. of comparison 35 heat-treated in 930 degree-Cx30s, crystal grain was set to about 30 micrometers. Since it became big and rough crystal grain, it not only has a bad influence on bending nature, but the stress relaxation characteristic declined a little.

[0047] Moreover, example No. of comparison 36-No. 41 are the example of comparison which added elements other than Sn into the Cu-nickel-Si-Mg-Zn alloy. Any [these] stress relaxation characteristic of an alloy is a stress relaxation characteristic of the same grade as example No. of comparison 27 with few additions of Sn, and it turns out that addition of these elements hardly contributes to stress relaxation.

[0048] Next, if it sees about the alloy which exists from the former, conventional example No. 42 are an Cu-nickel-Si alloy, and other alloying elements are not contained. In this case, since a stress relaxation characteristic does not contain the point which is not good, and Zn, a problem is in the heating detachability of Sn plating. Conventional example No. 43 are as point ** the material which added Sn and Zn into the Cu-nickel-Si system alloy. Although the heating detachability of Sn plating improves, the stress relaxation characteristic is equivalent to conventional example No. 41, and inadequate.

[0049] No. 44 are the material which added Mg and aimed at the improvement of a stress relaxation characteristic. Although the stress relaxation characteristic improves according to the effect of Mg, a problem is in bending nature. In order to obtain a stress relaxation characteristic equivalent to these conventional example No. 44, and good bending nature, it is attained by reducing the amount of Mg, adding Sn like example No. of this invention 2, and adding Zn which improves bending nature further. The heating detachability of Sn plating is also improved according to the Zn addition effect.

[0050]

[Example 2] Table 7 and Table 8 explain the 2nd example of this invention. As the alloy which consists of composition of example No. of this invention 2 shown in the above-mentioned example 1 is manufactured at the process depended table 7 and is shown in Table 8, the 2nd example Various characterization of F.A.R, and a (%) and a barricade (micrometer) was performed as TS(tensile strength)N/mm², EI(elongation) %, EC(conductivity) %IACS, bending nature, S.R.R(rate of stress relaxation) %, Sn

plating detachability, and punching nature. The evaluation method is the same as that of an example 1.

[Table 7]

	No	再結晶処理 ℃×s	冷間加工 加工率%	時効条件 ℃×hr	最終加工 加工率%	最終焼鈍 ℃×hr	
本 発 明 例	45	750×30	処理無し	515×2	0	処理無し	No. 2と同じ
	46	725×30	↑	↑	↑	↑	No. 18と同じ
	47	800×30	↑	↑	↑	↑	No. 19と同じ
	48	850×30	↑	↑	↑	↑	No. 20と同じ
	49	900×30	↑	↑	↑	↑	No. 21と同じ
	50	750×30	↑	535×2	↑	↑	
	51	↑	20	500×2	↑	↑	
	52	↑	処理無し	515×2	10	375×2	
	53	↑	↑	↑	20	350×2	
比 較 例	54	680×30	処理無し	515×2	0	処理無し	No. 34と同じ
	55	930×30	↑	↑	↑	↑	No. 35と同じ
	56	750×30	↑	400×2	↑	↑	
	57	750×30	↑	560×2	↑	↑	
	58	750×30	↑	515×2	33	350×2	
	59	750×30	↑	515×2	20	処理無し	

[Table 8]

	No	TS N/mm ²	EI %	EC %IACS	曲げ 加工性	S. R. R %	Snメッキ 剥離性	打ち抜き性	
								F. A. R(%)	バリ(μm)
本 発 明 例	45	670	16	39	B	18	剥離無し	45	6
	46	680	14	39	C	20	↑	46	6
	47	670	16	39	B	18	↑	44	7
	48	670	16	39	B	18	↑	41	9
	49	660	13	39	C	19	↑	39	11
	50	640	17	40	B	21	↑	46	7
	51	680	12	40	B	17	↑	49	5
	52	670	13	39	B	17	↑	47	7
	53	680	12	40	B	16	↑	50	5
比 較 例	54	680	12	39	D	22	剥離無し	45	8
	55	650	9	39	D	25	↑	40	12
	56	550	19	35	B	29	↑	31	14
	57	540	18	42	A	30	↑	34	11
	58	730	8	40	D	16	↑	53	3
	59	730	4	38	D	22	↑	61	2

[0051] Each example No. of this invention 45-No. 53 which is the alloy manufactured at the process of the example of this invention showed the outstanding property so that clearly from Table 7 and Table 8. However, example No. of comparison 54 had low heat treatment temperature, crystal grain was not uniform as a result, and bending nature deteriorated. Since example No. of comparison 55 heat-treated in 930 degree-Cx30s, crystal grain was set to about 30 micrometers. Since it was big and rough crystal grain, it not only has a bad influence on bending nature, but the stress relaxation characteristic declined a little.

[0052] Example No. of comparison 56 had low aging temperature, and the inadequate hatchet strength property deteriorated [the deposit]. The stress relaxation characteristic also declined sharply simultaneously. Conversely, No. 57 had high aging temperature, and since the sludge turned big and rough, the stress relaxation characteristic declined sharply. Example No. of comparison 58 are the example which performed cold working by the above working ratio specified by this invention after aging. Although the stress relaxation characteristic was excellent rather, bending nature fell. Although the rate of cold working after aging of example No. of comparison 59 is not high, it is the example which did not perform the postheat treatment. Elongation is low and not only bending nature fell, but the stress relaxation characteristic declined a little.

[0053]

[Effect of the Invention] As described above, the copper alloy of this invention deposits the compound of nickel and Si in Cu matrix, and does so the effect that the copper alloy which combines the outstanding mechanical property, conductivity, a stress relaxation characteristic, and bending nature is obtained, Sn, Mg, or by having carried out the amount addition of specification of the Zn further, having restricted S and O content, and having exceeded 1 micrometer and having set the grain size number to 25 micrometers or less. Since it excels in intensity, conductivity and a stress relaxation characteristic, and a bending moldability and excels also in the heating-proof detachability of Sn plating, or punching nature as a terminal and an object for connectors especially, it can respond to small and highly-efficient-izing which are an inclination in recent years suitably. Moreover, although this invention is suitable for a terminal and a connector use, the effect of offering a copper alloy suitable also as general electrical conducting materials, such as a switch and relay material, is done so.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Drawing explaining the examination of the stress relaxation of this invention example

[Description of Notations]

- 1 Sample
 - 2 Pedestal
 - 3 Attachment Component
 - 4 Block
-

[Translation done.]

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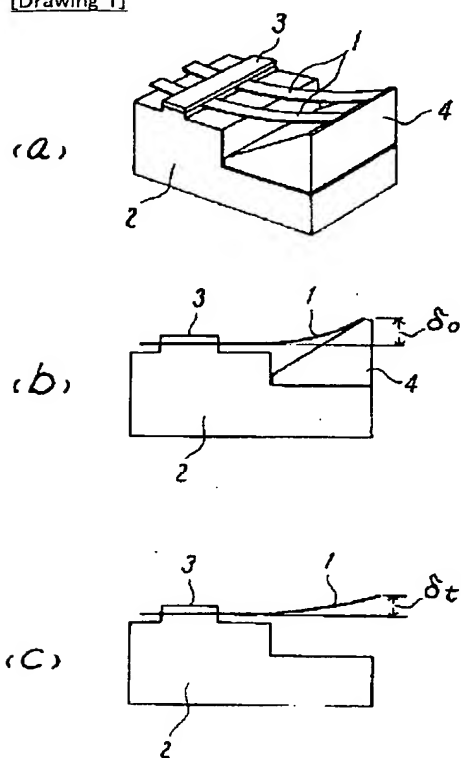
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DRAWINGS

[Drawing 1]



[Translation done.]

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(54) COPPER ALLOY FOR ELCTRICALLY CONDUCTIVE SPRING AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a copper alloy combining excellent mechanical properties, conductivity, stress relaxation characteristics and bending workability.

SOLUTION: This copper alloy is the one having a compsn. contg., as essential components, by weight, 1.0 to 3.5% Ni, 0.2 to 0.9% Si, 0.01 to 0.20% Mg and 0.05 to 1.5% Sn, in which each content of S and O is limited to <0.005%, and the balance Cu with inevitable impurities, and the grain size thereof is regulated to >1 to 25 μ m. Thus, this is suitable for terminals, connector materials and switch materials. Furthermore, as for the method for producing it, after cold working, recrystallization treatment is executed at 700 to 920° C.

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(54) 【発明の名称】 導電性ばね用銅合金及及びその製造方法

(57) 【要約】

【課題】 優れた機械的特性、伝導性、応力緩和特性と曲げ加工性を兼ね備えた銅合金を提供する。

【解決手段】 主成分としてNiを1.0~3.5wt%、Siを0.2~0.9wt%、Mgを0.01~0.20wt%、Snを0.05~1.5wt%含み、S、O含有量をそれぞれ0.005wt%未満に制限し、残部Cu及び不可避免の不純物からなり、その結晶粒度が1 μ mを越え25 μ m以下であることを特徴とする導電性ばね用銅合金であり、端子、コネクタ材、スイッチ材に適するものである。また製造方法は冷間加工後に再結晶処理を700~920℃で行うものである。

【特許請求の範囲】

【請求項1】 主成分としてNiを1.0～3.5wt%、Siを0.2～0.9wt%、Mgを0.01～0.20wt%、Snを0.05～1.5wt%含み、S、O含有量をそれぞれ0.005wt%未満に制限し、残部Cu及び不可避免の不純物からなり、その結晶粒度が1 μ mを越え25 μ m以下であることを特徴とする導電性ばね用銅合金。

【請求項2】 主成分としてNiを1.0～3.5wt%、Siを0.2～0.9wt%、Mgを0.01～0.20wt%、Snを0.05～1.5wt%、Znを0.2～1.5wt%含み、S、O含有量をそれぞれ0.005wt%未満に制限し、残部Cu及び不可避免の不純物からなり、その結晶粒度が1 μ mを越え25 μ m以下であることを特徴とする導電性ばね用銅合金。

【請求項3】 請求項1又は2に記載の銅合金に、さらに0.005～0.3wt%Ag、0.01～0.5wt%Mn、それぞれ0.005～0.2wt%のFe、Cr、0.05～2.0wt%Co、0.005～0.1wt%Pの中から選ばれ1種または2種以上を総量で0.005wt%～2.0wt%含むことを特徴とする導電性ばね用銅合金。

【請求項4】 請求項1又は2に記載の銅合金に、さらに0.005～0.1wt%Pb、0.005～0.03wt%Biの1種または2種を総量で0.005～0.13wt%含むことを特徴とする導電性ばね用銅合金。

【請求項5】 請求項1又は2に記載の銅合金に、さらに0.005～0.3wt%Ag、0.01～0.5wt%Mn、それぞれ0.005～0.2wt%のFe、Cr、0.05～2.0wt%Co、0.005～0.1wt%Pの中から選ばれ1種または2種以上、及び0.005～0.1wt%Pb、0.005～0.03wt%Biの1種または2種を総量で0.005wt%～2.0wt%含むことを特徴とする導電性ばね用銅合金。

【請求項6】 端子、コネクタ材、スイッチ材のいずれかに用いられるものであることを特徴とする請求項1乃至5のいずれかに記載の導電性ばね用銅合金。

【請求項7】 冷間加工後に再結晶処理を700～920℃で行うことを特徴とする請求項1乃至6のいずれかに記載の導電性ばね用銅合金の製造方法。

【請求項8】 冷間加工後に再結晶処理を700～920℃で行った後に、420～550℃で時効処理を行うことを特徴とする請求項1乃至6のいずれかに記載の導電性ばね用銅合金の製造方法。

【請求項9】 冷間加工後に再結晶処理を700～920℃で行い、さらに25%以下の冷間加工を行った後に、420～550℃で時効処理を行うことを特徴とする

【請求項10】 冷間加工後に再結晶処理を700～920℃で行い、次に25%以下の冷間加工、420～550℃での時効処理を行った後に、さらに25%以下の冷間加工、及び低温焼鈍を行うことを特徴とする請求項1乃至6のいずれかに記載の導電性ばね用銅合金の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、導電性ばね用銅合金及びその製造方法に関し、特に端子・コネクタ材、スイッチ材等に適する導電性ばね用銅合金とその製造方法に関する。

【0002】

【従来の技術】 従来より端子、コネクタ用材料として銅合金が用いられ、Cu-Zn系合金、耐熱性に優れたCu-Fe系合金、Cu-Sn系合金が多く用いられている。特に、自動車等の用途では安価なCu-Zn系合金が多く使用されているが、近年の自動車用端子、コネクタは小型化傾向が著しく、またエンジンルーム内などの過酷な環境にさらされる場合が多いため、Cu-Zn系合金ではもちろんのこと、Cu-Fe系合金、Cu-Sn系合金でも対応出来なくなっているのが現状である。

【0003】 このように、使用されている環境の変化に伴い、端子、コネクタ用材料に求められる特性もより厳しくなっている。このような用途に使用される銅合金には、応力緩和特性、機械的強度、熱伝導性、曲げ加工性、耐熱性、Snメッキの接続信頼性、マイグレーション特性など多岐に渡っているが、特に機械的強度や応力緩和特性、熱・電気の伝導性、曲げ加工性が重要な特性である。

【0004】 これらの厳しい要求特性を満たす銅系材料として、Cu-Ni-Si系合金が注目されており、例えば、特開昭61-127842号公報が知られている。しかしながら、このようなCu-Ni-Si系合金でも使用に耐え得ない状態に陥っている。具体的には部品の小型化、例えば一般的な箱型端子において、挿入されるオス端子のタブ幅が約2mmである090端子から約1mmである040端子へ小型化されると、バネ部の幅が1mm程度であり、このように部品が小型化されると、十分な接続強度を得ることが困難になっている。また、小型化に関連してバネ部での接続強度を確保するために、端子の構造にも多くの工夫がなされているが、その結果、材料に要求される曲げ加工性もより厳しくなっており、従来のCu-Ni-Siでは曲げ部にクラックが生じる場合も多い。応力緩和特性も同様であり、材料に負荷される応力の増大、使用環境の高温化により従来のCu-Ni-Si系合金では長時間の使用は不可能な

改善するためにMgの添加が有効であり、例えば、特開昭61-250134号公報、特開平5-59468号公報などにもMgの有効性が示されている。しかしながらMg添加により応力緩和特性は向上するものの、曲げ加工性が劣化し、180°密着曲げには耐え得ないものであり自動車コネクタなどに使用するには曲げ加工性の改善が不可欠である。また曲げ加工性を改善するための検討もされているが、これは強度の低い材料であるために所望の特性が得られないものであった。さらに、熱・電気の伝導性が悪いと、応力緩和特性が良くとも、自己発熱で応力緩和を促進するため、伝導性と応力緩和特性のバランスが重要である。

【0006】

【発明が解決しようとする課題】上述したように、曲げ加工性、応力緩和特性等について検討し、厳しい要求特性を満たす銅系材料が提案されているが、本発明は、優れた機械的特性、伝導性、応力緩和特性と曲げ加工性を兼ね備えた銅合金であり、端子、コネクタに好適な銅合金を提供するものである。

【0007】

【問題を解決するための手段】本発明は、上記課題を解決するもので、主成分としてNiを1.0~3.5wt%、Siを0.2~0.9wt%、Mgを0.01~0.20wt%、Snを0.05~1.5wt%含む、S、O含有量をそれぞれ0.005wt%未満に制限し、残部Cu及び不可避免の不純物からなり、その結晶粒度が1 μ mを越え25 μ m以下であることを特徴とする導電性ばね用銅合金である。また、上記構成において、本発明の特性に悪影響を与えない範囲で、他の添加元素、例えば0.2%未満のZnを添加しても差し支えないものである。また、本発明は、主成分としてNiを1.0~3.5wt%、Siを0.2~0.9wt%、Mgを0.01~0.20wt%、Snを0.05~1.5wt%、Znを0.2~1.5wt%含む、S、O含有量をそれぞれ0.005wt%未満に制限し、残部Cu及び不可避免の不純物からなり、その結晶粒度が1 μ mを越え25 μ m以下であることを特徴とする導電性ばね用銅合金である。

【0008】また、本発明は、上記の銅合金に、さらにAg、Mn、Fe、Cr、Co、Pの中から選ばれ1種または2種以上を総量で0.005wt%~2.0wt%含むことを特徴とする銅合金である。具体的には、主成分としてNiを1.0~3.5wt%、Siを0.2~0.9wt%、Mgを0.01~0.20wt%、Snを0.05~1.5wt%含む、さらに0.005~0.3wt%Ag、0.01~0.5wt%Mn、それぞれ0.005~0.2wt%のFe、Cr、0.05~2.0wt%Co、0.005~0.1wt%Pの中

0.5wt%未満に制限し、残部Cu及び不可避免の不純物からなり、その結晶粒度が1 μ mを越え25 μ m以下であることを特徴とする導電性ばね用銅合金である。また、主成分としてNiを1.0~3.5wt%、Siを0.2~0.9wt%、Mgを0.01~0.20wt%、Snを0.05~1.5wt%、Znを0.2~1.5wt%含む、さらに0.005~0.3wt%Ag、0.01~0.5wt%Mn、それぞれ0.005~0.2wt%のFe、Cr、0.05~2.0wt%Co、0.005~0.1wt%Pの中から選ばれ1種または2種以上を総量で0.005wt%~2.0wt%含む、S、O含有量をそれぞれ0.005wt%未満に制限し、残部Cu及び不可避免の不純物からなり、その結晶粒度が1 μ mを越え25 μ m以下であることを特徴とする導電性ばね用銅合金である。

【0009】また、本発明は、上記の銅合金に、さらにPb、Biの1種または2種を総量で0.005~0.13wt%含むことを特徴とする銅合金である。具体的には、主成分としてNiを1.0~3.5wt%、Siを0.2~0.9wt%、Mgを0.01~0.20wt%、Snを0.05~1.5wt%含む、さらに0.005~0.1wt%Pb、0.005~0.03wt%Biの1種または2種を総量で0.005~0.13wt%含む、S、O含有量をそれぞれ0.005wt%未満に制限し、残部Cu及び不可避免の不純物からなり、その結晶粒度が1 μ mを越え25 μ m以下であることを特徴とする導電性ばね用銅合金である。また、主成分としてNiを1.0~3.5wt%、Siを0.2~0.9wt%、Mgを0.01~0.20wt%、Snを0.05~1.5wt%、Znを0.2~1.5wt%含む、さらに0.005~0.1wt%Pb、0.005~0.03wt%Biの1種または2種を総量で0.005~0.13wt%含む、S、O含有量をそれぞれ0.005wt%未満に制限し、残部Cu及び不可避免の不純物からなり、その結晶粒度が1 μ mを越え25 μ m以下であることを特徴とする導電性ばね用銅合金である。

【0010】また、上記の銅合金に、さらにAg、Mn、Fe、Cr、Co、Pの中から選ばれ1種または2種以上、及びPb、Biの1種または2種を総量で0.005wt%~2.0wt%含むことを特徴とする銅合金である。具体的には、主成分としてNiを1.0~3.5wt%、Siを0.2~0.9wt%、Mgを0.01~0.20wt%、Snを0.05~1.5wt%含む、さらに0.005~0.3wt%Ag、0.01~0.5wt%Mn、それぞれ0.005~0.2wt%のFe、Cr、0.05~2.0wt%Co、0.005~0.1wt%Pの中から選ばれ1種または2種以上、及び0.005~0.1wt%Pb、0.0

ぞれ0.005wt%未満に制限し、残部Cu及び不可避免的な不純物からなり、その結晶粒度が $1\mu\text{m}$ を超え $25\mu\text{m}$ 以下であることを特徴とする導電性ばね用銅合金である。また、主成分としてNiを1.0~3.5wt%、Siを0.2~0.9wt%、Mgを0.01~0.20wt%、Snを0.05~1.5wt%、Znを0.2~1.5wt%含み、さらに0.005~0.3wt%Ag、0.01~0.5wt%Mn、それぞれ0.005~0.2wt%のFe、Cr、0.05~2.0wt%Co、0.005~0.1wt%Pの中から選ばれ1種または2種以上、及び0.005~0.1wt%Pb、0.005~0.03wt%Biの1種または2種を総量で0.005wt%~2.0wt%含み、S、O含有量をそれぞれ0.005wt%未満に制限し、残部Cu及び不可避免的な不純物からなり、その結晶粒度が $1\mu\text{m}$ を超え $25\mu\text{m}$ 以下であることを特徴とする導電性ばね用銅合金である。

【0011】また、本発明の上記銅合金は、端子、コネクタ材、スイッチ材のいずれかに用いられるものであることを特徴とするものである。また、本発明は、冷間加工後に再結晶処理を $700\sim 920^{\circ}\text{C}$ で行うことを特徴とする導電性ばね用銅合金の製造方法である。また、冷間加工後に再結晶処理を $700\sim 920^{\circ}\text{C}$ で行った後に、 $420\sim 550^{\circ}\text{C}$ で時効処理を行うことを特徴とする導電性ばね用銅合金の製造方法である。また、冷間加工後に再結晶処理を $700\sim 920^{\circ}\text{C}$ で行い、さらに25%以下の冷間加工を行った後に、 $420\sim 550^{\circ}\text{C}$ で時効処理を行うことを特徴とする導電性ばね用銅合金の製造方法である。さらに、冷間加工後に再結晶処理を $700\sim 920^{\circ}\text{C}$ で行い、次に25%以下の冷間加工、 $420\sim 550^{\circ}\text{C}$ での時効処理を行った後に、さらに25%以下の冷間加工、及び低温焼鈍を行うことを特徴とする導電性ばね用銅合金の製造方法である。

【0012】

【作用】本発明の銅合金は、Cuマトリックス中にNiとSiの化合物を析出させ、適当な機械的強度及び熱・電気導電性を有する銅合金に、Sn、Mg、Znを特定量添加し、S、O含有量を制限して、かつ結晶粒度を $1\mu\text{m}$ を超え $25\mu\text{m}$ 以下として応力緩和特性と曲げ加工性を改善することを骨子としている。本発明者らは、この銅合金成分の含有量を詳細に規定することで実用的に優れた特性を有する導電性ばね用銅合金、特に端子、コネクタ用として優れた特性を有する材料を実現させることができることを見だし、その結果本発明の銅合金を得たものである。

【0013】以下に本発明の銅合金の成分限定理由を説明する。CuにNiとSiを含有させるとNi-Si化合物を作り、これをCu中に析出させ強度及び導電率を

Ni量が3.5wt%を超えると casting、熱間加工時に強度上昇に寄与しない析出が生じ含有量に見合う強度を得ることができないばかりか、熱間加工性、曲げ加工性にも悪影響を与えることになる。Si量は析出するNiとSiの化合物が Ni_2Si 相であると考えられるため、Ni量を決定すると最適なSi含有量が決まる。Si量が0.2wt%未満であるとNi量が少なくなると同様十分な強度を得ることができない。逆にSi含有量が0.9wt%を超えるときもNi量が多い場合と同様の問題が生ずる。好ましくは、Niを1.7~2.8wt%、Siを0.4~0.7wt%に調整することが望ましい。

【0014】Mg、Snは本発明の銅合金を構成する重要な添加元素である。これらの元素は相互に関係しあって良好な特性バランスを実現している。次に、これら元素の限定理由を説明する。Mgは応力緩和特性を大幅に改善するが、曲げ加工性には悪影響を及ぼす。応力緩和特性の観点からは、0.01wt%以上で含有量は多いほどよい。逆に曲げ加工性の観点からは、含有量が0.20wt%を超えると良好な曲げ加工性を得ることは困難である。このような観点から、Mgの含有範囲は0.01~0.20wt%において良好なバランスを示す。曲げ加工性の観点からより好ましいMgの含有範囲は、0.01~0.1wt%である。

【0015】さらに、Snを加えることにより、良好な曲げ加工性を保ったまま、より応力緩和特性を改善できることを見いだした。Snは、応力緩和特性の改善効果を有するものの、その効果はMgほど大きくないが、Mgと相互に関係しあって良好な特性バランスを示すものである。Snを1.5wt%を超えて含有すると、熱及び電気伝導性が劣化し、実用上問題を来す。Sn含有量はMg量との兼ね合いもあるが、0.05~1.5wt%で良好な特性バランスを示す。具体的には、Mgが0.01~0.05wt%の場合には、Snは0.8~1.5wt%が好ましく、Mg量が0.05~0.1wt%の場合には、Snは0.05~0.8wt%が好ましい。

【0016】Znは応力緩和特性に寄与しないが、曲げ加工性を改善することができる。Znを0.2~1.5wt%、好ましくは0.3~1.0wt%含有することにより、Mgを最大0.20wt%まで含有させても実用上問題ないレベルの曲げ加工性を達成できる。またZnはSnメッキやハンダメッキの耐熱剥離性、マイグレーション特性を改善する効果を有し、打ち抜き加工性を改善する作用も有し、実用上の観点からZnを0.2wt%、好ましくは0.3wt%以上含有させることが望ましい。打ち抜き加工性を改善する元素としては、Pb、Biがあるが、Pb、Biは多量に添加すると熱間

ある。その上限は熱・電気伝導性を考慮し、1.5wt%、好ましくは1.0wt%である。なお、本実施例からも、Mgとの共添でより良い傾向にあることが示されている。

【0017】以上、Mg、Sn、Znの添加範囲を限定した理由を詳述したが、これらの元素の限定範囲内でそれぞれ最大含有量とすることは好ましくない。実用上、最もバランスの良好な含有量の範囲は、Mg:0.05~0.15wt%、Sn:0.2~0.5wt%、Zn:0.3~0.8wt%である。

【0018】次に、Ag、Mn、Fe、Cr、Co、Pの含有量の範囲を限定した理由を説明する。Ag、Mn、Fe、Cr、Co、Pは、加工性を改善するという点で類似の機能を有しているものであり、Ag、Mn、Fe、Cr、Co、Pの中から選ばれ1種または2種以上を0.005wt%~2.0wt%含有させるものである。

【0019】Agは、耐熱性を上げ、強度を上昇させると同時に、結晶粒の粗大化を阻止し、曲げ加工性を改善することができる。従来より、Cu-Ni-Si系合金の強度を上昇させるために種々の第三元素を添加することが試みられている処であるが、それらは大幅に導電率を下げたり、曲げ成形性が劣化し、電子機器用途として好ましくない特性が現れるものであった。本発明は、強度を向上し、且つその他の特性に悪影響を及ぼさない元素の検討を繰り返した結果、Agが有効であることを見いだしたものである。含有量が0.005wt%未満であるとその効果が現れず、逆に0.3wt%を超えて含有すると特性上の悪影響はないものの、コスト高となるので、Agの最適含有量は0.005~0.3wt%であり、より好ましくは0.005~0.1wt%である。

【0020】Mnは、強度を上昇させると同時に熱間加工性を改善する効果があり、0.01wt%未満であるとその効果が小さく、0.5wt%を超えて含有しても、含有量に見合った効果が得られないばかりでなく、伝導性を劣化させる。よってMnの最適含有範囲は、0.01~0.5wt%であり、より好ましくは0.03~0.3wt%である。

【0021】Fe、Crは、Siと結合し、Fe-Si化合物、Cr-Si化合物を形成し強度を上昇させる。またNiとの化合物を形成せずに銅マトリックス中に残存するSiをトラップし、導電性を改善する効果がある。Fe-Si化合物、Cr-Si化合物は析出硬化能が低いため、多くの化合物を生成させることは得策でない。また、0.2wt%を超えて含有すると曲げ加工性が劣化してくる。これらの観点から、Fe、Crを含有する場合の添加量は、0.005~0.2wt%であ

し、機械的強度を向上させる。Coは、Niに比し高価であるため、本発明ではCu-Ni-Si系合金を利用しているが、コスト的に許されるのであれば、Cu-Co-Si系やCu-Ni-Co-Si系を選択しても良い。Cu-Co-Si系は時効析出させた場合に、Cu-Ni-Si系より機械的強度、導電性共に僅かに良くなる。したがって熱・電気伝導性を重視される部材には有効である。また、Co-Si化合物は析出硬化能が僅かに高いため、応力緩和特性も若干改善される傾向にある。これらの観点から、Coを添加する場合の最適添加量は、0.05~2.0wt%である。

【0023】Pは、強度を上昇させると同時に導電性を改善する効果を有する。多量の含有は粒界析出を助長して曲げ加工性を低下させる。よってPを添加する場合の最適含有範囲は、0.005~0.1wt%であり、より好ましくは0.005~0.05wt%である。これらを2種以上同時に添加する場合には、求められる特性に応じて適宜決定すれば良いが、耐熱性、Snメッキ、ハンダメッキ耐熱剥離性、伝導性などの観点から総量で0.005~2.0wt%とした。

【0024】次に、Pb、Biの含有量の範囲を限定した理由を説明する。Pb、Biは、打ち抜き加工性を改善するもので、Pb、Biの1種または2種を0.005~0.13wt%含有するものである。Pbは打ち抜き加工性を改善する添加元素である。近年のプレス高速化にともない、端子用材料にはより優れた加工性が求められている。Pbは銅マトリックス中に分散し、破壊の起点になるため打ち抜き加工性を改善する。Pb量が0.005wt%未満であると特性改善効果がなく、0.1wt%を超えて添加すると熱間加工性を低下させるばかりでなく、曲げ加工性をも劣化させるため、0.005~0.1wt%が最適であり、より好ましくは0.005~0.05wt%である。Biも打ち抜き加工性を改善する添加元素である。0.005wt%未満であると特性改善効果が小さく、0.03wt%を超えて添加するとPbと同様の特性低下を来す。よってBiの最適含有範囲は、0.005~0.03wt%であり、より好ましくは0.005~0.02wt%である。

【0025】これらAg、Mn、Fe、Cr、Co、Pの中から選ばれ1種または2種以上、及びPb、Biの1種または2種を同時に含有する場合には、求められる特性に応じて適宜決定すれば良いが、耐熱性、Snメッキ、ハンダメッキ耐熱剥離性、伝導性などの観点から総量で0.005~2.0wt%とした。

【0026】次に、S、O含有量を0.005wt%未満に制限した理由を説明する。通常、工業的な銅材料にはS、O₂等が微量含まれるが、本発明はこれらの含

のである。Sは、熱間加工性を悪化させる元素であり、その含有量を0.005wt%未満と規定することで、熱間加工性を向上させる。特にS含有量を0.002wt%未満にすることが望ましい。Oは、その含有量が0.005wt%以上であると、Mgが酸化されて曲げ加工性が劣化する。O含有量を0.005wt%以下、特に0.002wt%未満にすることが望ましい。以上説明したS、Oは、通常の銅系材料中に微量に含有される場合が多いが、本発明の銅合金においては特に重要であり、その含有量を規定することで優れた特性が得られるもので、端子、コネクタ用材料に好適な特性を実現することを見いだしたのである。

【0027】上述した本発明の銅合金の構成において、その特性を好適に実現するためには、結晶粒度が $1\mu\text{m}$ を越え $25\mu\text{m}$ 以下とすることが必要である。結晶粒度が $1\mu\text{m}$ 以下であると、再結晶組織において混粒と成り易く、曲げ加工性が低下すると同時に応力緩和特性が低下する。逆に結晶粒度が $25\mu\text{m}$ を越えて成長しても、曲げ加工性に悪影響を及ぼす。従って、結晶粒度は $1\mu\text{m}$ を越え $25\mu\text{m}$ 以下に調整する必要がある。

【0028】次いで、本発明の銅合金の製造法について説明する。本発明の銅合金は、冷間加工、例えば冷間圧延した後に、再結晶と溶体化させる目的で熱処理を行い、直ちに焼き入れを行う。また必要に応じて時効処理を行うものである。本発明の銅合金における結晶粒度を $1\mu\text{m}$ を越え $25\mu\text{m}$ 以下の範囲に調整するためには、再結晶処理の条件を詳細に制御する必要がある。700℃未満の温度での熱処理は、混粒となり易く、920℃を越える温度では結晶粒が粗大に成長しやすいので、冷間加工後に再結晶処理を700～920℃で行うものである。また、冷却速度は出来るだけ素早く、10℃/s以上の速度で冷却することが望ましい。

【0029】次に、時効熱処理の条件については、時効温度が420℃未満であると、析出硬化量が不十分であり、充分な特性を引き出すことができない。逆に550℃を越える温度で処理すると、析出相が粗大に成長し、強度が低下するばかりでなく、応力緩和特性も低下させてしまう。よって、時効処理温度は420～550℃とした。さらには、応力緩和特性は析出相の状態に大きく影響を受けることが判っており、時効強度がピークを示す温度近傍が最良条件である。一方、曲げ加工性は時効強度がピークを示す温度から若干過時効側で熱処理を行うことが望ましい。このような観点から好ましくは460～530℃での処理が最適である。

【0030】また、冷間加工後に再結晶処理（溶体化）を700～920℃で行い、さらに冷間加工（25%以下）を行った後に420～550℃で時効処理を行うものである。後に述べる実施例では、溶体化後直ちに時

せない断面減少率25%以下の加工が望ましい。また、冷間加工後に再結晶処理（溶体化）を700～920℃で行い、冷間加工（25%以下）、420～550℃で時効処理を行った後に、さらに25%以下の冷間加工、及び低温焼鈍を行うものである。このように時効処理後に冷間加工を施しても構わない。この場合は本発明の特徴である曲げ加工性を劣化させないために、断面減少率25%以下の加工が望ましい。更に、前述の時効処理後の冷間加工を行う場合には、その後に比較的低温での焼鈍を行うことが推奨される。この焼鈍をバッチ式焼鈍で行う場合には、250～400℃の温度で0.5～5h、走間焼鈍で行う場合には600～800℃の温度で5～60sの条件で行うことが望ましい。この焼鈍は冷間加工で導入された転位を再配列し、結果的には転位の移動を抑制する作用を有する。従って、前述の冷間加工を行った場合には、焼鈍を行うことにより応力緩和特性を改善することができる。必要に応じて最終の熱処理前若しくは後にテンションレベラーやローラーレベラー等の矯正を行っても良い。

【0031】

【発明の実施の形態】本発明の銅合金は、優れた機械的強度、曲げ加工性、応力緩和特性、Snメッキ剥離性、打ち抜き性等を有し、特に、端子・コネクタ材、スイッチ材、リレー材等、一般導電材料等に求められる特性を備えたものであり、実施例により詳細に説明する。

【0032】

【実施例1】本発明の第1の実施例を表1～6に示し説明する。表1は本発明例の合金組成、表2、表3は比較例、従来例の合金組成であり、表4は本発明例合金の特性、表5、表6は比較例、従来例の合金の特性を示すものである。なお、なお、表中の矢印は上の欄と同じことを示すものであり、(*)は耐力値が低く、試料セット段階で塑性変形を起こしたために試験中止したものである。

【0033】まず、高周波溶解炉にて、表1～表3に記す組成の合金を溶解し、冷却速度6℃/sで铸込んだ。铸塊のサイズは厚さ30mm、幅100mm、長さ150mmである。次にこれらの铸塊を900℃で熱間圧延をしてから、速やかに冷却を行った。表面の酸化膜を除去するため厚さ9mmまで面削してから、冷間圧延により厚さ0.25mmに加工した。この後、供試材を再結晶と溶体化させる目的で、750℃で30sの熱処理を行い、直ちに15℃/s以上の冷却速度で焼き入れを行った。時効処理は、不活性雰囲気中で515℃×2時間の熱処理を施し、試験に供する材料とした。

【0034】製造した材料からサンプリングして、結晶粒度を測定し、TS（引張り強度）N/mm²、EI（伸び）%、EC（導電率）%IACS、曲げ加工性、

性評価を行った。

【0035】結晶粒度、即ち結晶粒の大きさは、JIS H0501に準じ、比較法と切断法を併用し観察を行った。比較法では試験片を顕微鏡観察（75倍または200倍）して測定した。切断法では加工方向に平行な板厚断面で測定を行った。引っ張り強度はJIS Z2241で、熱・電気の伝導性を示す値として、導電率をJIS H0505に準じて測定した。

【0036】曲げ加工性の評価は、内側曲げ半径がORの180°密着曲げを行った。評価の指標は、

- A. しわもなく良好
 - B. 小さなしわが観察される
 - C. 大きなしわが観察されるが、クラックには至っていない
 - D. 微細なクラックが観察される
 - E. 明瞭にクラックが観察される
- の5段階で評価し、評価C以上を実用上問題の無いレベルと判断した。

【0037】応力緩和特性の評価は、日本電子材料工業会標準規格であるEMAS-3003に準拠して行った。ここで片持ちブロック式を採用し、表面最大応力が450N/mm²となるように負荷応力を設定し、150℃の恒温槽で試験を行った。表4～表6には、1000hr試験後の緩和率（S. R. R）で示した。

【0038】応力緩和の試験方法の片持ちブロック法について、図1（a）（b）（c）に示す。図1（a）は斜視図、（b）は側面図であり、サンプル（1）の一方は基台（2）に保持部材（3）で片持ち状態に支持し、もう一方はブロック（4）によりサンプル（1）に歪み

δo（初期たわみ変位）を与えた状態にする。この状態でサンプル（1）を150℃に所定時間（本実施例では1000hr）加熱する。所定時間経過後、図1（c）の側面図に示すように、ブロック（4）を取り除いた状態での歪みδt（永久たわみ変位）を測定し、応力緩和率（%）は次式で求めた。

$$\text{応力緩和率 (\%)} = (\delta t / \delta o) \times 100$$

なお、初期たわみ変位は、表面最大応力が所定の値（450N/mm²）になるよう、ヤング率、板厚等から計算するものである（計算方法はEMAS-3003による）。

【0039】Snメッキの加熱剥離性は、1μmの光沢Snメッキを施した試験片を150℃×1000時間の大気加熱をしてから、180度の密着曲げ、および曲げ戻しをした後、その部分のメッキ剥離を目視にて評価した。半田の剥離が認められる場合、表4～6に「有」と記した。

【0040】打ち抜き性は、金型（SKD11製）で打ち抜き試験（1mm×5mmの角孔を設ける）を行うことにより調べた。そして5001回目から10000回目の打ち抜き分から20個無作為に抽出したサンプルの打ち抜き面を観察して破断部の厚さを測定した。表4～6には試験片の厚さに対する破断部の厚さの割合の平均値を%表示で示す（表中でF. A. Rと表示）。バリ測定についても同様に、5001回目から10000回目の打ち抜き部分から20個無作為に抽出したサンプルのバリの高さを接触式形状測定機で求め、平均値を表に記載した。

【表1】

	No	Ni	Si	Mg	Sn	Zn	S	O	その他	結晶粒度
本 発 明 例	1	1.5	0.34	0.07	0.31	0.49	0.002	0.001		5
	2	1.9	0.48	0.08	0.30	0.48	0.002	0.001		↑
	3	2.5	0.60	0.08	0.30	0.49	0.002	0.001		↑
	4	3.0	0.75	0.07	0.31	0.50	0.002	0.001		↑
	5	2.0	0.48	0.04	0.30	0.50	0.002	0.001		↑
	6	1.9	0.48	0.03	0.85	0.49	0.002	0.001		↑
	7	2.0	0.47	0.08	0.87	0.50	0.002	0.001		↑
	8	2.0	0.46	0.16	0.29	0.09	0.002	0.001		↑
	9	2.0	0.47	0.16	0.30	1.10	0.002	0.001		↑
	10	2.0	0.48	0.08	0.30	1.07	0.002	0.001		↑
	11	1.9	0.46	0.04	0.87	0.10	0.002	0.001		↑
	12	2.0	0.48	0.07	0.85	1.10	0.002	0.001		↑
	13	1.5	0.47	0.08	0.33	0.50	0.002	0.001	Co0.5	↑
	14	1.9	0.48	0.08	0.31	0.49	0.002	0.001	Co0.1	↑
	15	2.0	0.48	0.08	0.32	0.49	0.002	0.001	Ag0.03	↑
	16	2.0	0.48	0.07	0.32	0.49	0.002	0.001	Pb0.03	↑
	17	2.0	0.47	0.08	0.33	0.50	0.002	0.001	Cr0.007	↑
	18	1.9	0.48	0.07	0.32	0.48	0.002	0.001		2
	19	2.0	0.48	0.06	0.33	0.49	0.002	0.001		10
	20	2.0	0.46	0.08	0.33	0.50	0.002	0.001		15

【表2】

	No	Ni	Si	Mg	Sn	Zn	S	O	その他	結晶粒度
比較例	22	0.8	0.18	0.08	0.34	0.50	0.002	0.001		5
	23	3.8	0.95	0.08	0.33	0.49	0.002	0.001		↑
	24	2.0	0.47	0.003	0.33	0.49	0.002	0.001		↑
	25	2.0	0.48	0.002	0.99	0.50	0.002	0.001		↑
	26	1.9	0.47	0.25	0.33	1.25	0.002	0.001		↑
	27	2.0	0.48	0.03	0.002	0.50	0.002	0.001		↑
	28	2.0	0.48	0.08	2.04	0.50	0.002	0.001		↑
	29	2.1	0.47	0.08	0.31	5.09	0.002	0.001		↑
	30	2.0	0.47	0.07	0.33	0.49	0.002	0.001	Fe0.35	↑
	31	1.9	0.48	0.08	0.32	0.48	0.002	0.001	Pb0.25	↑
	32	1.9	0.46	0.09	0.33	0.49	0.011	0.001		↑
	33	2.0	0.48	0.08	0.32	0.50	0.002	0.007		↑
	34	2.0	0.47	0.08	0.31	0.50	0.002	0.001		≤1
	35	2.0	0.48	0.08	0.32	0.49	0.002	0.001		30

【表3】

	No	Ni	Si	Mg	Sn	Zn	S	O	その他	結晶粒度
比較例	36	2.0	0.47	0.07	0.002	0.49	0.002	0.001	Cr0.10	5
	37	1.9	0.48	0.08	0.001	0.48	0.002	0.001	Mn0.39	↑
	38	2.0	0.48	0.08	0.002	0.50	0.002	0.001	B0.008	↑
	39	2.0	0.47	0.08	0.001	0.50	0.002	0.001	Al0.50	↑
	40	2.0	0.48	0.08	0.001	0.50	0.002	0.001	Ti0.10	↑
	41	2.0	0.48	0.08	0.002	0.49	0.002	0.001	In0.10	↑
従米例	42	2.5	0.60	—	—	—	—	—		
	43	1.9	0.50	—	0.4	0.9	—	—		
	44	2.7	0.65	0.17	—	—	—	—		

【表4】

	No	TS N/mm ²	El %	EC %IACS	曲げ 加工性	S. R. R %	Snメッキ 剥離性	打ち抜き性	
								F. A. R(%)	バリ(μm)
本 発 明 例	1	610	16	39	B	22	剥離無し	42	9
	2	670	16	39	B	18	↑	45	6
	3	680	15	38	B	17	↑	46	6
	4	680	14	38	C	17	↑	50	5
	5	660	16	40	B	22	↑	44	7
	6	680	16	33	B	18	↑	46	7
	7	680	15	32	B	14	↑	47	8
	8	670	16	38	C	14	↑	47	6
	9	670	16	36	B	14	↑	51	4
	10	670	16	37	B	18	↑	50	4
	11	680	15	33	C	18	↑	41	10
	12	680	15	31	B	14	↑	54	3
	13	710	15	42	B	15	↑	49	4
	14	700	15	40	B	16	↑	47	4
	15	680	16	39	B	18	↑	45	7
	16	670	16	39	B	19	↑	55	2
	17	660	15	41	B	19	↑	45	8
	18	680	14	39	C	20	↑	46	6
	19	670	16	39	B	18	↑	44	7
	20	670	16	39	B	18	↑	41	9
	21	660	13	39	C	19	↑	39	11

【表5】

	No	TS N/mm ²	El %	EC %IACS	曲げ 加工性	S. R. R %	Snメッキ 剥離性	打ち抜き性	
								F. A. R(%)	バリ(μm)
比 較 例	22	480	19	51	A	—(+)	剥離無し	31	19
	23	680	14	38	D	17	↑	49	4
	24	670	16	40	B	33	↑	40	11
	25	680	16	32	B	31	↑	42	11
	26	670	15	34	D	13	↑	58	2
	27	670	16	42	B	24	↑	45	5
	28	690	15	23	B	13	↑	46	6
	29	680	17	29	B	18	↑	56	2
	30	530	18	43	D	—(+)	↑	37	17
	31	熱間加工中に割れが生じたため製造中止							
	32	熱間加工中に割れが生じたため製造中止							
	33	670	10	40	D	23	剥離無し	46	6
	34	680	12	39	D	22	↑	45	8
	35	650	9	39	D	25	↑	40	12

【表6】

	No	TS N/mm ²	EI %	EC %IACS	曲げ 加工性	S.R.R %	Snメッキ 剥離性	打ち抜き性	
								F.A.R (%)	バネ (μm)
比較例	36	650	17	42	B	24	剥離無し	44	8
	37	670	15	35	B	25	↑	46	7
	38	670	16	40	B	25	↑	41	11
	39	670	16	35	B	23	↑	47	8
	40	660	15	40	B	26	↑	46	9
	41	680	16	39	B	24	↑	44	10
従来例	42	670	17	46	B	34	剥離有り	38	13
	43	650	16	38	B	33	剥離無し	37	13
	44	680	11	44	D	19	剥離有り	40	11

【0041】表4から明らかなように、本発明例1～21は、TS（引張り強度）、EI（伸び）、EC（導電率）、曲げ加工性、S.R.R（応力緩和率）、Snメッキ剥離性、打ち抜き性の各種特性の何れも優れた特性を示していることが判る。

【0042】一方、Ni-Si量の少ない比較例No. 22は、目的とする強度が得られず、打ち抜き加工性も他の材料と比較して劣っている。逆にNi-Si量の多い比較例No. 23は、Ni-Si量の少ない本発明例No. 4と比較し強度の点では差はないが、曲げ加工性では劣化傾向を示した。即ち、本発明で規定する量以上のNi-Siを添加することは、曲げ加工性が劣るので、端子・コネクタ用として不適である。

【0043】Mgの添加量が少ない比較例No. 24は、本発明例のNo. 2、No. 5と比較し、応力緩和特性が大幅に劣っている。これと同じ理由で比較例No. 25は本発明例No. 6、No. 7より劣っている。このことは、従来のCu-Ni-Si合金（従来例No. 42）にSnを単独で添加しても、応力緩和特性には大きな改善効果を期待できないことを示すものであり、従来のSn入りCu-Ni-Si合金（従来例No. 43）の特性と一致する。

【0044】Mgの添加量が、本発明の規定量以上である比較例No. 26は、曲げ加工性が劣化している。これは端子・コネクタ材としては不適である。曲げ加工性を若干改善できるZnを1wt%以上添加しても良好な曲げ加工性は確保できなかった。Snの添加量が少ない比較例No. 27は、本発明例のNo. 2と比較し、応力緩和特性の点で劣っている。逆にSnの添加量が多い比較例No. 28は、Mgの効果と相まり、今回製造を行った中で最も優れた応力緩和特性を示した組成の一つであった。しかしながら、導電率が最も低くなり、バランス的に優れているとは言えない。Znの添加量が多い比較例No. 29も導電率が低くなり、特性バランスに優れない。

【0045】Feの添加量が規定量以下である比較例No.

及ぼした。Pbの添加量を多くした比較例No. 31は熱間加工中に割れを生じ、正常に製造することが出来なかった。その他、Sが本発明範囲外にある比較例No. 32は、熱間加工時に割れが生じ、その後の特性評価を行えなかった。また、Oが多い比較例No. 33は、Mgの酸化物が生成しており、曲げ加工性が劣化した。

【0046】比較例No. 34は、再結晶させるための焼鈍を680℃×30sで行った。その結果、平均結晶粒は1μm以下で、比較的大きな結晶粒と小さな結晶粒が混在する組織となった。不均一な組織のため、曲げ加工性を行う試験片を採取する場所によっては、クラックを生ずる結果となった。逆に、比較例No. 35は930℃×30sで熱処理を行ったため、結晶粒はおおよそ30μmとなった。粗大な結晶粒となったため、曲げ加工性に悪影響を及ぼすばかりでなく、若干応力緩和特性も低下した。

【0047】また比較例No. 36～No. 41は、Cu-Ni-Si-Mg-Zn合金にSn以外の元素を添加した比較例である。これらいずれの合金の応力緩和特性もSnの添加量が少ない比較例No. 27と同程度の応力緩和特性であり、これらの元素の添加は応力緩和にほとんど寄与しないことが判る。

【0048】次に、従来から存在する合金についてみると、従来例No. 42は、Cu-Ni-Si合金であり、その他の添加元素は含まれていない。この場合、応力緩和特性が良くない点と、Znを含まないため、Snメッキの加熱剥離性に問題がある。従来例No. 43は先述のとおり、Cu-Ni-Si系合金にSnとZnを添加した材料である。Snメッキの加熱剥離性は改善されているが、応力緩和特性は従来例No. 41と同等であり不十分である。

【0049】No. 44は、Mgを添加し、応力緩和特性の改善を図った材料である。Mgの効果により応力緩和特性は改善されているが、曲げ加工性に問題がある。この従来例No. 44と同等の応力緩和特性と良好な曲げ加工性を得るためには、本発明例No. 2のように

より、Snメッキの加熱剥離性も改善される。

【0050】

【実施例2】本発明の第2の実施例を表7、表8で説明する。第2の実施例は、上記実施例1に示した本発明例No. 2の組成からなる合金を、表7による工程で製造して、表8に示すように、TS（引張り強度）N/m

m²、EI（伸び）%、EC（導電率）%IACS、曲げ加工性、S. R. R（応力緩和率）%、Snメッキ剥離性、打ち抜き性としてF. A. R（%）、バリ（μm）の各種特性評価を行った。評価方法は実施例1と同様である。

【表7】

	No	再結晶処理 ℃×s	冷間加工 加工率%	時効条件 ℃×hr	最終加工 加工率%	最終焼鈍 ℃×hr	
本 発 明 例	45	750×30	処理無し	515×2	0	処理無し	No. 2と同じ
	46	725×30	↑	↑	↑	↑	No. 18と同じ
	47	800×30	↑	↑	↑	↑	No. 19と同じ
	48	850×30	↑	↑	↑	↑	No. 20と同じ
	49	900×30	↑	↑	↑	↑	No. 21と同じ
	50	750×30	↑	535×2	↑	↑	
	51	↑	20	500×2	↑	↑	
	52	↑	処理無し	515×2	10	375×2	
	53	↑	↑	↑	20	350×2	
比 較 例	54	680×30	処理無し	515×2	0	処理無し	No. 34と同じ
	55	930×30	↑	↑	↑	↑	No. 35と同じ
	56	750×30	↑	400×2	↑	↑	
	57	750×30	↑	560×2	↑	↑	
	58	750×30	↑	515×2	33	350×2	
	59	750×30	↑	515×2	20	処理無し	

【表8】

	No	TS N/mm ²	EI %	EC %IACS	曲げ 加工性	S. R. R %	Snメッキ 剥離性	打ち抜き性	
								F. A. R(%)	バリ(μm)
本 発 明 例	45	670	16	39	B	18	剥離無し	45	6
	46	680	14	39	C	20	↑	46	6
	47	670	16	39	B	18	↑	44	7
	48	670	16	39	B	18	↑	41	9
	49	660	13	39	C	19	↑	39	11
	50	640	17	40	B	21	↑	46	7
	51	680	12	40	B	17	↑	49	5
	52	670	13	39	B	17	↑	47	7
	53	680	12	40	B	16	↑	50	5
比 較 例	54	680	12	39	D	22	剥離無し	45	8
	55	650	9	39	D	25	↑	40	12
	56	550	19	35	B	29	↑	31	14
	57	540	18	42	A	30	↑	34	11
	58	730	8	40	D	16	↑	53	3
	59	730	4	38	D	22	↑	61	2

【0051】表7、表8から明らかなように、本発明例の工程で製造した合金である本発明例No. 45～N

55は930℃×30sで熱処理を行ったために、結晶粒はおよそ30μmとなった。粗大な結晶粒であるた

が不十分なため強度特性が劣化した。同時に応力緩和特性も大幅に低下した。逆にNo. 57は時効温度が高く、析出物が粗大化したため、応力緩和特性が大幅に低下した。比較例No. 58は時効後に本発明で規定する以上の加工率で冷間加工を行った例である。応力緩和特性はむしろ優れるが、曲げ加工性が低下した。比較例No. 59は時効後の冷間加工率は高くないが、その後熱処理を行わなかった例である。伸びが低く曲げ加工性が低下したばかりでなく、応力緩和特性も若干低下した。

【0053】

【発明の効果】以上記述したように、本発明の銅合金は、Cuマトリックス中にNiとSiの化合物を析出させ、Sn、Mg、或いは更にZnを特定量添加し、S、O含有量を制限して、かつ結晶粒度を $1\mu\text{m}$ を越え $25\mu\text{m}$ 以下としたことにより、優れた機械的特性、伝導性、応力緩和特性と曲げ加工性を兼ね備えた銅合金が得

られるという効果を奏するものである。特に、端子・コネクタ用として、強度や伝導性、応力緩和特性、曲げ成形性に優れ、またSnメッキの耐加熱剥離性や打ち抜き性にも優れるものであるから、近年の傾向である小型、高性能化に好適に対応できる。また本発明は端子・コネクタ用途に好適なものであるが、その他スイッチ、リレー材等、一般導電材料としても好適な銅合金を提供するという効果を奏するものである。

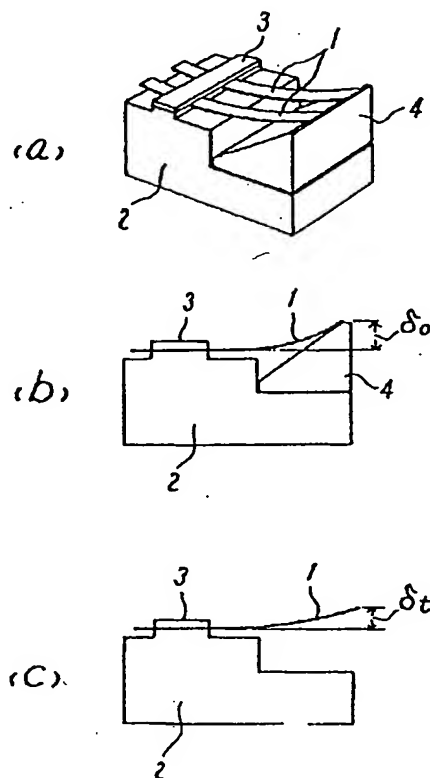
【図面の簡単な説明】

【図1】 本発明実施例の応力緩和の試験を説明する図

【符号の説明】

- 1 サンプル
- 2 基台
- 3 保持部材
- 4 ブロック

【図1】



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